1969

The Kinetics of Alkylation of Isobutane With Propylene Using a Sulfuric Acid Catalyst.

John Randolph Langley
Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_disstheses/1602

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
This dissertation has been microfilmed exactly as received

LANGLEY, John Randolph, 1942-
THE KINETICS OF ALKYLATION OF ISOBUTANE WITH PROPYLENE USING A SULFURIC ACID CATALYST.

The Louisiana State University and Agricultural and Mechanical College, Ph.D., 1969
Engineering, chemical

University Microfilms, Inc., Ann Arbor, Michigan
THE KINETICS OF ALKYLATION OF ISOBUTANE WITH PROPYLENE USING A SULFURIC ACID CATALYST

A Dissertation
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemical Engineering

by

John Randolph Langley
B.S., Louisiana State University, 1965
M.S., Louisiana State University, 1967

May 1969

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
To my wife, Sandra, for her love, patience, and hard work.
ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. R. W. Pike for his guidance throughout this research. His close attention and time given to the latter stages of this research and to the completion of this dissertation are appreciated.

The author wishes to thank Mr. Jose Paniza and Mr. H. A. Schuyten for their assistance in the chromatographic analyses in this work. Appreciation is also expressed to Mr. D. D. Esch for his aid in conducting the residence time distribution test.

The advice given by Dr. P. A. Bryant on the statistical analysis of the data is also appreciated.

The author is very grateful to Mr. Jack Wade of the Esso Research Laboratories of Baton Rouge for his help in calibration of the gas chromatograph. The author also thanks Mr. S. R. Bethea and Mr. W. C. Jones of the Baytown Research Research Division of the Esso Research and Engineering Company, Baytown, Texas, for their aid in calibration of the gas chromatograph.

The author has appreciated the financial assistance given him by the National Science Foundation under grant GK-744, by the Esso Research Laboratories under their research assistantship which the author was given, and the Charles E. Coates Memorial Fund of the L. S. U. Foundation for funds to pay a portion of the typing cost of the dissertation.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The author thanks the Computer Research Center of Louisiana State University for the computer time given to this research.

Finally, the author wishes to thank his wife, Sandra, for the time given to the typing and proofreading of this dissertation.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xv</td>
</tr>
<tr>
<td>CHAPTER I - INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>I. Commercial Interests and Facts</td>
<td>1</td>
</tr>
<tr>
<td>Importance as an Industrial Process</td>
<td></td>
</tr>
<tr>
<td>Reactants and Product Description</td>
<td></td>
</tr>
<tr>
<td>Catalysts Used</td>
<td></td>
</tr>
<tr>
<td>Conditions of Operation</td>
<td></td>
</tr>
<tr>
<td>II. Uniqueness of the Alkylation Medium</td>
<td>3</td>
</tr>
<tr>
<td>III. Previous Research on Mechanisms and Kinetics of Isobutane-Olefin-Alkylation</td>
<td>4</td>
</tr>
<tr>
<td>Mechanism</td>
<td></td>
</tr>
<tr>
<td>The Schmerling Theory of Alkylation</td>
<td></td>
</tr>
<tr>
<td>Other Mechanism Studies</td>
<td></td>
</tr>
<tr>
<td>Kinetics</td>
<td></td>
</tr>
<tr>
<td>Operating Variables</td>
<td></td>
</tr>
<tr>
<td>Mixing and Mass Transfer in Liquid-Liquid Heterogeneous Reaction Systems</td>
<td></td>
</tr>
<tr>
<td>Summary</td>
<td></td>
</tr>
<tr>
<td>IV. Statement of the Problem</td>
<td>51</td>
</tr>
<tr>
<td>CHAPTER II - ISOBUTANE-PROPENE ALKYLATION</td>
<td>53</td>
</tr>
<tr>
<td>MECHANISTIC AND KINETIC MODELS</td>
<td></td>
</tr>
<tr>
<td>I. Introduction</td>
<td>53</td>
</tr>
<tr>
<td>II. Modifications of Schmerling Theory for the Mechanistic Model</td>
<td>56</td>
</tr>
<tr>
<td>Octane Formation</td>
<td></td>
</tr>
</tbody>
</table>
Nonane Formation
Decane Formation
Undecane Formation
Other Reactions

III. Rate Equations and the Mathematical Model 63

Derivation of the Mathematical Model
Temperature Dependence of the Reaction Rate Constants

IV. Estimation of the Concentrations of the Various Species in the Catalyst Phase 81

Isobutane Concentration in the Catalyst Phase
Propylene Concentration in the Acid Phase
Other Paraffin Concentrations in the Acid Phase
Estimation of Ionic Intermediate Concentrations
Concentrations of the Olefinic Intermediates
Summary

CHAPTER III - EXPERIMENTAL AND ANALYTICAL EQUIPMENT AND PROCEDURES 95

I. Alkylation Pilot Unit 95

Reactor Temperature Control Loop
Mechanical Seal Lubrication and Cooling Loop
Tracer Injection Valve
The Pressure System

II. Sampling System 106

III. Analytical Tools 112

Gas Chromatography Equipment and Techniques
Titration Procedures
Radioactivity Measuring Techniques

IV. Operating Procedures 119

Preparation of Feed Blend

vi

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computer Program EX</td>
<td>234</td>
</tr>
<tr>
<td>Flow Diagram of Computer Program PR</td>
<td>239</td>
</tr>
<tr>
<td>Computer Program PR</td>
<td>242</td>
</tr>
<tr>
<td><strong>APPENDIX C - HYDROCARBON PHASE CONCENTRATION PREDICTION MODEL</strong></td>
<td></td>
</tr>
<tr>
<td>Derivation of Prediction Model</td>
<td>245</td>
</tr>
<tr>
<td>Flow Diagram of Computer Program LS</td>
<td>251</td>
</tr>
<tr>
<td>Computer Program LS</td>
<td>255</td>
</tr>
<tr>
<td><strong>VITA</strong></td>
<td>259</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1.1</td>
<td>Initiation Reactions</td>
<td>54</td>
</tr>
<tr>
<td>2-1.2</td>
<td>Primary Reactions</td>
<td>54</td>
</tr>
<tr>
<td>2-1.3</td>
<td>Self-Alkylation Reactions</td>
<td>54</td>
</tr>
<tr>
<td>2-1.4</td>
<td>Destructive Reactions</td>
<td>55</td>
</tr>
<tr>
<td>2-2.1</td>
<td>Material Balance on Reactants and Associated Consumption Rates</td>
<td>65</td>
</tr>
<tr>
<td>2-2.2</td>
<td>Product Formation Equations</td>
<td>66</td>
</tr>
<tr>
<td>2-2.3</td>
<td>Olefinic Intermediate Rate Equations</td>
<td>67</td>
</tr>
<tr>
<td>2-2.4</td>
<td>Carbonium Ion Rate Equations</td>
<td>68</td>
</tr>
<tr>
<td>2-2.5</td>
<td>Special Rate Equations</td>
<td>69</td>
</tr>
<tr>
<td>2-3.1</td>
<td>Rate Constant Expressions</td>
<td>79</td>
</tr>
<tr>
<td>3-1</td>
<td>Accuracy of the Gas Chromatographic Analytical Technique</td>
<td>118</td>
</tr>
<tr>
<td>3-2</td>
<td>Summary of Experimental Conditions</td>
<td>131</td>
</tr>
<tr>
<td>4-1</td>
<td>Results of the Least Squares Fits of the Rate Constants over the Range of 81 to 135°F, and with a 95% H₂SO₄ Catalyst</td>
<td>141</td>
</tr>
<tr>
<td>4-2</td>
<td>Rate Constants Calculated from Experimental Data from Runs with a 95% Catalyst Concentration in the Range of 81 to 135°F.</td>
<td>146</td>
</tr>
<tr>
<td>4-3</td>
<td>Comparison of Experimental and Predicted Values for the Rate Constants at 65°F. Using a 95% H₂SO₄ Catalyst</td>
<td>181</td>
</tr>
<tr>
<td>4-4</td>
<td>The Weight Percent Product Distribution Based on Gas Chromatograph Analyses</td>
<td>182</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4-5</td>
<td>The Predicted Values of $k_{10}$ and $k_{13}$ Compared to the Values Experimentally Determined Using a 90% $\text{H}_2\text{SO}_4$ Catalyst</td>
<td>196</td>
</tr>
<tr>
<td>4-6</td>
<td>Comparison of Alkylation Data from Cupit et al. (7) with That of Experiment Nine</td>
<td>210</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3-1</td>
<td>Pilot unit flow diagram</td>
<td>96</td>
</tr>
<tr>
<td>3-2</td>
<td>Pilot unit reactor and settler</td>
<td>97</td>
</tr>
<tr>
<td>3-3</td>
<td>Feed tank</td>
<td>99</td>
</tr>
<tr>
<td>3-4</td>
<td>Reactor</td>
<td>100</td>
</tr>
<tr>
<td>3-5</td>
<td>Acid settler</td>
<td>102</td>
</tr>
<tr>
<td>3-6</td>
<td>Caustic wash vessel</td>
<td>103</td>
</tr>
<tr>
<td>3-7</td>
<td>Tracer injection valve</td>
<td>105</td>
</tr>
<tr>
<td>3-8</td>
<td>Emulsion sample valve assembly</td>
<td>108</td>
</tr>
<tr>
<td>3-9</td>
<td>High-pressure sample vial</td>
<td>109</td>
</tr>
<tr>
<td>3-10</td>
<td>Probe sampler</td>
<td>110</td>
</tr>
<tr>
<td>3-11</td>
<td>Gas chromatograph and recorder</td>
<td>113</td>
</tr>
<tr>
<td>3-12</td>
<td>Calculation of peak area</td>
<td>116</td>
</tr>
<tr>
<td>3-13</td>
<td>Packard liquid scintillation spectrometer</td>
<td>120</td>
</tr>
<tr>
<td>3-14</td>
<td>Feed blend mix tank</td>
<td>122</td>
</tr>
<tr>
<td>3-15</td>
<td>Step one: Sampling from emulsion sample valve assembly</td>
<td>127</td>
</tr>
<tr>
<td>3-16</td>
<td>Step two: Post-pressurizing the sample vial</td>
<td>128</td>
</tr>
<tr>
<td>3-17</td>
<td>Step three: Obtaining hydrocarbon sample from vial with the probe sampler</td>
<td>129</td>
</tr>
<tr>
<td>3-18</td>
<td>Step four: Injection of hydrocarbon sample into gas chromatograph</td>
<td>130</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>3-19</td>
<td>Residence time distribution plot of alkylation pilot unit</td>
<td>134</td>
</tr>
<tr>
<td>4-1</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_1 ), and the corresponding least squares fit</td>
<td>147</td>
</tr>
<tr>
<td>4-2</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_9 ), and the corresponding least squares fit</td>
<td>148</td>
</tr>
<tr>
<td>4-3</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_{10} ), and the corresponding least squares fit</td>
<td>150</td>
</tr>
<tr>
<td>4-4</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_{11} ), and the corresponding least squares fit</td>
<td>152</td>
</tr>
<tr>
<td>4-5</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_{12} ), and the corresponding least squares fit</td>
<td>154</td>
</tr>
<tr>
<td>4-6</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_{13} ), and the corresponding least squares fit</td>
<td>155</td>
</tr>
<tr>
<td>4-7</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_{14} ), and the corresponding least squares fit</td>
<td>156</td>
</tr>
<tr>
<td>4-8</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_{15} ), and the corresponding least squares fit</td>
<td>158</td>
</tr>
<tr>
<td>4-9</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_{16} ), and the corresponding least squares fit</td>
<td>159</td>
</tr>
<tr>
<td>4-10</td>
<td>Arrhenius plot of the experimentally determined values of the reaction rate constant, ( k_{18} ), and the corresponding least squares fit</td>
<td>161</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>4-11</td>
<td>162</td>
<td></td>
</tr>
<tr>
<td>4-12</td>
<td>166</td>
<td></td>
</tr>
<tr>
<td>4-13</td>
<td>167</td>
<td></td>
</tr>
<tr>
<td>4-14</td>
<td>169</td>
<td></td>
</tr>
<tr>
<td>4-15</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>4-16</td>
<td>173</td>
<td></td>
</tr>
<tr>
<td>4-17</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td>4-18</td>
<td>176</td>
<td></td>
</tr>
<tr>
<td>4-19</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>4-20</td>
<td>194</td>
<td></td>
</tr>
</tbody>
</table>

The predicted pounds of product yield per pound of olefin fed as a function of temperature using 95% \( \text{H}_2\text{SO}_4 \) and 0.143 lb./lb. feed

The predicted weight fraction of \( \text{iC}_7 \) and \( \text{iC}_8 \) in the product as a function of temperature using 95% \( \text{H}_2\text{SO}_4 \) and 0.143 lb./lb. feed

The predicted weight fraction of \( \text{C}_3 \), \( \text{iC}_5 \) and \( \text{C}_6 \) in the product as a function of temperature using 95% \( \text{H}_2\text{SO}_4 \) and 0.143 lb./lb. feed

The predicted weight fraction of \( \text{C}_9 \) and \( \text{C}_{10} \) in the product as a function of temperature using 95% \( \text{H}_2\text{SO}_4 \) and 0.143 lb./lb. feed

The predicted pounds of product yield per pound of olefin fed as a function of the weight fraction of propylene in the feed at 105% using 95% \( \text{H}_2\text{SO}_4 \)

The predicted weight fraction of \( \text{iC}_7 \) and \( \text{iC}_8 \) in the product as a function of the weight fraction of propylene in the feed at 105°F and using 95% \( \text{H}_2\text{SO}_4 \)

The predicted weight fraction of \( \text{C}_3 \), \( \text{iC}_5 \) and \( \text{C}_6 \) in the product as a function of the weight fraction of propylene in the feed at 105°F and using 95% \( \text{H}_2\text{SO}_4 \)

The predicted weight fraction of \( \text{C}_9 \) and \( \text{C}_{10} \) in the product as a function of the weight fraction of propylene in the feed at 105°F and using 95% \( \text{H}_2\text{SO}_4 \)

The values of \( k_1 \) obtained at a catalyst strength of 90% \( \text{H}_2\text{SO}_4 \) compared with the least squares fit of the values obtained at 95% \( \text{H}_2\text{SO}_4 \)

The values of \( k_2 \) obtained at a catalyst strength of 90% \( \text{H}_2\text{SO}_4 \) compared with the least squares fit of the values obtained at 95% \( \text{H}_2\text{SO}_4 \)
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-21</td>
<td>The values of $k_{11}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$</td>
<td>197</td>
</tr>
<tr>
<td>4-22</td>
<td>The values of $k_{12}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$</td>
<td>199</td>
</tr>
<tr>
<td>4-23</td>
<td>The values of $k_{14}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$</td>
<td>200</td>
</tr>
<tr>
<td>4-24</td>
<td>The values of $k_{15}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$</td>
<td>202</td>
</tr>
<tr>
<td>4-25</td>
<td>The values of $k_{16}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$</td>
<td>203</td>
</tr>
<tr>
<td>4-26</td>
<td>The values of $k_{18}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$</td>
<td>205</td>
</tr>
</tbody>
</table>
ABSTRACT

Commercial catalytic alkylation of isobutane with \( C_3 \) to \( C_5 \) olefins is an important source of high octane motor fuel. Both sulfuric and hydrofluoric acid are used as catalysts; however, the sulfuric acid process is the more widely used. Because liquid-liquid, complex reactions are involved, the theoretical knowledge of the process has lagged behind the commercial development.

The most significant theoretical contribution has been the Schmerling carbonium ion mechanism. Other researchers have sought to modify certain portions of this theory; however, it still remains the most comprehensive description of the alkylation reactions available. In addition, many research contributions have been more closely allied to the effect of operating variables on the product quality. The work in this area has been so voluminous that several survey articles have been devoted to it.

What has been needed is a detailed kinetic study of olefin-isobutane alkylation with sulfuric acid catalyst. This type of study has not been performed due to the physical nature of the reaction medium and the complex chemistry involved. Until recently there has not been sufficient theoretical and experimental developments to perform such a work as this.
As Schmerling's mechanism is the most comprehensive one available, it served as the basis for the mathematical model. In addition, modifications were introduced to account for \( C_9 \) and \( C_{10} \) formation. Schmerling was not explicit about the reaction paths to form these species. These modifications were consistent with the remainder of the theory.

A mathematical model was derived by solving the steady state rate equations for the rate constants of the modified Schmerling mechanism. This resulted in a total of eighteen rate constants and eighteen rate equations of the form:

\[
k_i = \frac{f(r_{C_j}, r_{C_k}, \ldots)}{f'([C_k], [C_1], \ldots)}
\]

where \( k_i \) is the reaction rate constant, \( r_j \) is the rate of formation of species \( C_j \) per unit volume of catalyst, and \( C_k \) is the concentration of species \( C_k \) - moles per unit volume of catalyst.

The species concentrations are those of the saturated products, reactants, olefinic intermediates, or ionic intermediates. The model was to be considered valid if the resulting rate constants obeyed Arrhenius' theory.

To obtain the necessary data isobutane was alkylated with propylene in an ideally mixed, continuous-flow, stirred reactor. The alkylation was carried out under the following conditions:
65°F. to 135°F., 90% to 95% H₂SO₄, 12.5 to 22.4% by weight propylene in the feed, olefin space velocity of 0.104 to 0.184 vol. olefin/vol. catalyst - hr., 60% acid in emulsion, and a flat blade turbine speed of 1,700 RPM. A hydrocarbon residence time of 52 minutes was used.

The reactor effluent was analyzed on a programmed temperature gas chromatograph with squalane coated capillary column and flame ionization detector. The results were the composition of the hydrocarbon species present in weight percent.

The mathematical model was found to be valid in the range of 81°F. to 135°F. using a 95% H₂SO₄ catalyst since the rate constants obeyed the Arrhenius theory. The resulting first order rate constants ranged from 2 x 10⁴ to 1 x 10⁶ sec.⁻¹; the second order rate constants ranged from 2 x 10⁵ to 1 x 10¹⁸ cc./gm. mole-sec.

The predictions obtained from the model included: (1) yield (lb. products/lb. C₃⁻ fed) increased both with temperature and olefin feed concentration increase; (2) the dimethylpentane product concentration remained constant with increase in temperature but increased with olefin feed concentration; and (3) the octanes (chiefly trimethylpentanes) decreased with increase of both temperature and olefin feed concentration. In general, due to the combined effects of reduced concentrations of octanes and increased yields of heavier products, lower temperatures and olefin feed concentrations favored...
a more commercially desirable product.

The results obtained at 65°F. and 95% H₂SO₄ indicated a significant departure from the predictions of the mathematical model. It is believed that this was due to a change in reaction mechanism and gave high rates of formation of C₉ and C₁₀. There was an apparent change in selectivity of the catalyst when the concentration was lowered to 90% H₂SO₄. This resulted in increased rates of formation of C₉ and C₁₀ and decreased rates of formation of C₅, C₆ and C₈.
CHAPTER I

INTRODUCTION

I. Commercial Interests and Facts

Importance as an Industrial Process

Catalytic alkylation of isobutane with various olefins, principal of which is butene, as an industrial process received its impetus for development by World War II. Being a source of high-octane fuel, its production level had reached 150,000 barrels per day at the end of the war due almost totally to aviation needs (7). Due to lower peace-time needs this figure was cut in half right after the war (7), but by 1960 the production capacity of the United States had reached 350,000 b.p.d. (2). The growth of this process points out its importance to the refining industry.

Reactants and Product Description

Generally the alkylation reaction may be considered the reaction of isobutane with an olefin to yield mainly the primary product described as that one which would arise from the combination of one molecule of isobutane and one of the olefin, with other secondary products, both heavier and lighter, being formed to a somewhat lesser extent.

For example, the alkylation of isobutane with butene-1 or butene-2 would result in a product with trimethylpentanes and dimethylhexanes predominating. However, other components from
isopentane to a dodecane series would be present in significant quantities (7).

**Catalysts Used**

For isobutane-olefin alkylation the two catalysts generally used are sulfuric and hydrofluoric acid. Both are protonic acids and there are various reasons concerning handling, reclaiming, etc., which makes one more or less desirable over the other. Sulfuric acid, however, has historical precedence (15) and as of 1962 maintained a lead of about three to one in terms of capacity (7).

**Conditions of Operation**

In commercial processes using sulfuric acid the temperature (assuming the most common case as having butene as the olefin) is generally kept in the range of 45°F. to 60°F. for optimum product quality. For a hydrofluoric acid this figure is somewhat higher - averaging about 80°F. Higher temperatures with sulfuric acid are undesirable due to increased polymer formation (15).

The optimum sulfuric acid concentration as to peak product quality (octane number, etc.) obtained is about 95-96% H₂SO₄ (27); however, the usable range appears to lie between the limits of 99% and 86%. Above this range SO₃ reacts with isobutane and beginning at about 88% and below the acid degrades too rapidly for use (7).

The percent acid in emulsion is generally kept in the range of 50% or above to insure an acid continuous emulsion. This type of emulsion is desired to produce the highest possible interfacial area of hydrocarbon exposed per volume of hydrocarbon (7).
Isobutane is fed to the reactor in excess of that required for the primary combination of isobutane and the olefin. Normally in terms of volumes, the ratio of isobutane to olefin generally lies in the range of 6:1 to 10:1 (15). This is to minimize the chance of high concentrations of the olefin within the reactor which would cause polymerization of the olefin.

A high degree of mixing is also employed to keep the emulsion fine and minimize the chances of polymer formation. If sufficient mass transfer area is not available the more acid soluble (relative to isobutane) olefin will migrate to acid phase in far greater quantities than isobutane; thus, product degradation will occur.

The olefin space velocity, the volume of olefin fed per volume of catalyst per hour, is another process variable which is important. Low space velocities are desirable from the standpoint of product quality. The general range of these velocities is generally around 0.1 to 0.4 (15).

II. Uniqueness of the Alkylation Medium

The isoparaffin reactants and products are relatively insoluble in both sulfuric and hydrofluoric acid. Because of this two liquid phases are always present. This physical property of the system makes it impossible to directly trace the course of the reaction as the reactants and products are only measurable in the hydrocarbon phase, whereas the bulk of the reaction is considered to proceed within the catalyst phase. A further complication to the picture is the fact that
the olefins are much more soluble in the acid phase than is the isopara-
affin (23). For this reason, the rate of mass transfer of the isoparaaffin
into the catalyst phase is probably important when considering reaction
rates. However, as there exist no measurements of the reaction rate
constants, the chemical reaction rates and mass transfer rates are
not readily separable (7).

III. Previous Research on Mechanisms and Kinetics
of Isobutane - Olefin Alkylation

Research on this type of alkylation (isobutane-olefin) has
largely centered on the sulfuric acid catalyst system. The scope of
the various research problems has included studies of mechanism,
kinetics and the effect of operating variables on the product quality.

Mechanism

Various studies have been performed and theories presented
on the subject of mechanism; however, the theoretical presentation
of Louis Schmerling (29) has been the most widely accepted base for
mechanistic work. Schmerling has based his mechanism on the car-
bonium ion theory of reaction; thus, a presentation of this theory as
it applies to isobutane-olefin alkylation will be presented as a
prelude to a detailed discussion of Schmerling's theory.

The only adequate, overall mechanism proposed for the
alkylation of isoparaffins with olefins is based upon the carbonium
ion theory of reaction (29). According to this mechanism, carbonium
ions make up the bulk of the reaction intermediates. Thus, any
kinetic study of such a system must necessarily be a kinetic study of
carbonium ion reactions either directly or indirectly.

The simplest carbonium ion is the positively charged derivative
of methane - CH₃⁺. All other carbonium ions are derivatives of
this species - with one or more of the hydrogen atoms being replaced
by an organic group (3). Thus, for a cation to be considered a car-onium ion, the charge must be considered to be "centered" on a
carbon with only three bonds (even though it is probably delocalized
to some extent), i.e., the ion must have an even number of electrons.

The particular carbonium ion considered to be the "classic"
among carbonium ions is the tertiary-triphenylmethyl carbonium ion.
Baeyer (3) studied the action of triphenylmethanol in sulfuric acid.
To explain the salt-like behavior (conductivity, color, etc.) of such
a solution, a "carbonium valency" between the organic and inorganic
groups was proposed. In this case the groups were the triphenylmethyl
group and the hydrogen sulfate group and was shown as follows:

\[
(C₆H₅)₃C \ldots \ldots HSO₄
\]

where the above symbol (\ldots\ldots) implies this type of association.
Later work (3) gave evidence that the bond between the two groups
was indeed ionic, implying that the positively charged "carbonium"
ions were relatively stable enough so that the solutions exhibited
electrolytic character. The organic cation and the inorganic anion
may be expressed as

\[(C_6H_5)_3C^+(HSO_4^-)\]  

much like an inorganic salt in solution. The association between the organic and the inorganic groups in sulfuric acid-catalyzed alkylation is much the same as above. However, the phenyl groups are replaced by other, generally simpler, groups such as the methyl groups resulting in

\[(CH_3)_3C^+(HSO_4^-)\]  

The primary difference between a) and b) is due to the difference in stability between the two cations. A mixture of tertiary isobutanol and sulfuric acid would exhibit much less electrolytic character due to an organic cation-inorganic anion action than one of triphenylmethanol and sulfuric acid, since the latter organic cation is much more stable.

This relative stability of carbonium ions must be considered in alkylation reactions as many different types of carbonium ions must exist at one time or another to explain the various reaction products. In the simplest sense, relative stability may be correlated to the relative delocalization of the charge on the species. The more delocalized the charge the more nearly neutral the species behaves, and thus the more stable it is. By this line of reasoning, the primary (denoted as to the carbon having lost the hydride ion) carbonium
ions would be the least stable of the species, the tertiary ions the most stable, with the secondary ions occupying the middle ground.

If two competing reactions involve say forming a secondary carbonium ion as an intermediate in one and a tertiary in the other, the reaction forming these tertiary ions would, on the basis of stability, be the predominant of the two. In this manner carbonium ion stability would be expected to affect the various reactions in alkylation.

Another factor which governs the stability of a carbonium ion is the nature of the adjacent groups to the carbon "bearing" the charge (3). Since the charge in this case is positive, adjacent groups which tend to be electron repelling, such as saturated organic groups, tend to be stabilizing influences. (Adjacent phenyl rings in addition to this action also allow the charge to be distributed about them giving further stability due to "resonance.")

Then, too, the size of the ion is a factor, as the larger the ion, the more surface area for the positive charge to spread out upon - the surface of the ion being considered somewhat like the surface of a conductor (3). Also, on saturated hydrocarbons, for example, with each additional carbon there should be correspondingly less area available per electron; thus a positive charge would relieve electron repulsion on large ions.

Thus, generally the larger the tertiary ion, the more stable it should be. So the tertiary 2,4-dimethylpentyl ion would be expected to be longer lived than its "little brother," the tertiary butyl ion, and
the reaction

\[
\begin{array}{c}
C \\
C-C^+ + C-C-C-C-C \rightarrow C-C^+ + C-C-C-C^+ - C
\end{array}
\]

would be expected to proceed. Consequently, in the alkylation of isobutane with propylene (or butylene, etc.) the isobutane must be present in large excess. This large excess may be considered a rate driving force, causing the above reaction to proceed in reverse.

The influence of stability and this rate driving force would definitely cause the reaction

\[
\begin{array}{c}
C \\
C-C + C-C^+ - C \rightarrow C-C^+ + C-C-C
\end{array}
\]

to proceed. The reverse of this reaction would not be expected as, in addition to stability arguments, hydrogen from a secondary position is less readily abstracted than one from a tertiary position (29).

A reaction such as

\[
\begin{array}{c}
C \\
C-C + R^+ \rightarrow C-C^+ + R
\end{array}
\]

where \( R \) is a large tertiary ion is less easily explained. However, in alkylation such a reaction is generally assumed to occur. Stability arguments would imply also that this type of reaction would proceed
slowly. The driving force for this reaction, therefore, would be the large excess of isobutane present.

Stability criteria may also be applied to the formation of larger (relative to the isobutyl ion) carbonium ions from a smaller ion and an olefin molecule. For example, the formation of a dimethyl-pentyl ion would be expected in the isobutane-propylene system to proceed as (intermediate isomerization of the C7 ion is not shown)

\[
\begin{align*}
\text{C} &+ \text{C}=\text{C} + \text{C} = \text{C} \rightarrow \text{C} = \text{C} - \text{C} - \text{C} - \text{C} \\
\text{C} &+ \text{C} = \text{C} + \text{C} = \text{C} \rightarrow \text{C} = \text{C} - \text{C} - \text{C} - \text{C}
\end{align*}
\]

An alternate path involving two other species present in the system would be

\[
\begin{align*}
\text{C} = \text{C} + \text{C} = \text{C} + \text{C} = \text{C} \rightarrow \text{C} = \text{C} - \text{C} - \text{C} - \text{C} \rightarrow \text{C} = \text{C} - \text{C} - \text{C} - \text{C}
\end{align*}
\]

The fact, however, that this would involve the reaction of a secondary ion would not lend credence to the reaction proceeding in this manner, as the secondary ion would not be long lived enough to reach an appreciable concentration as compared to the tertiary ion.

Bethell and Gold (3) emphasize the importance on the formation of carbonium ions, i.e.,

\[
\text{RX} \rightarrow \text{R}^{+} + \text{X}^{-}
\]

when considering any reaction involving carbonium ion intermediates.
This concern may be quite valid when the starting compound is a salt (or ester) such as RX, and the general reaction is

\[ RX + MA \rightarrow RA + MX \]

which may be broken down into the following steps:

\[ RX \rightarrow R^+ + X^- \]

\[ R^+ + MA \rightarrow RA + M^+ \]

\[ M^+ + X^- \rightarrow MX \]

In alkylation, however, originally there is no organic salt - rather there is the pure organic compound, say propylene, and the acid which supplies the anion, say sulfuric acid - and what may be considered to be a compound analogous to the one above, may be formed in the initial reaction:

\[ \text{C}=\text{C}-\text{C} + \text{H}_2\text{SO}_4 \rightarrow \text{C}-\text{C}-\text{C} (\text{HSO}_4^-) \]

In other carbonium ion reactions in the alkylation system, the primary sequence may be shown as

\[ C_m = + iC_4^+ \xrightarrow{k_2} C_{m+4}^+ \]

\[ C_{m+4}^+ + iC_4 \xrightarrow{k_5} iC_4^+ + C_{m+4} \]
If associations and dissociations of the esters are included

\[ iC_4X \xrightarrow{k_1} iC_4^+ + X^- \]

\[ C_m^- + iC_4^+ \xrightarrow{k_2} C_{m+4}^+ \]

\[ C_{m+4}^+ + X^- \xrightarrow{k_3} C_{m+4}X \]

\[ C_{m+4}X \xrightarrow{k_4} C_{m+4}^+ + X^- \]

\[ C_{m+4}^+ + iC_4 \xrightarrow{k_5} C_{m+4}^+ + iC_4^+ \]

\[ iC_4^+ + X^- \xrightarrow{k_6} iC_4X \]

four additional reactions are added. However, the sum of the reactions is still the primary sequence as above. If any of the above esters were to enter into any reaction in which the dissociation is not represented by

\[ C_iX \xrightarrow{} C_i^+ + X^- \]

then the formation and dissociation steps for that ester must remain in this sequence. However, in alkylation, this type of ester reaction would be the only possible one to occur. For the inclusion of these reactions, the overall rates of formation for the sequence shown would be

\[ r_{iC_4X} = -k_1[iC_4X] + k_6[iC_4^+][X^-] \]
The net rates of formation of the esters, equations a and b, may be taken as zero. This may be done since no ester is found in an alkylate product, and no noticeable volume change of the acid occurs. Also, the reactions represented by equations a and b are the only reactions in which each of these esters takes part. (The same may not be done for the ion formations, as these are not the only reactions in which they appear.) If this is done and equations a and b substituted into c, d, e, f and g, then the end result is:

\[ r_{iC_4} = -k_2 [iC_4^-][C_m=] + k_5 [C_{m+4}^+][iC_4] \]
which is precisely the result obtained when ester reactions are not
considered. Thus, consideration of ester reactions of the type above
generates two rate constants for each ester considered, but only one
rate equation may be written expressing the relationship these two
rate constants bear in alkylation, i.e.,

\[ r_{iC_4X} = 0 = -k_4[iC_4^+X] + k_6[iC_4^+]X^- \]

Neither of these constants will appear in another rate equation inde­
dependently of the other. These rate constants, therefore, cannot be
solved for in a kinetic analysis of alkylation. Consequently, a
kinetic model derived on the basis of a steady state series of rate
equations will not be able to handle the ester reactions regardless of
their importance in the sequence.

The only other type of reaction involving carbonium ions to
occur in this alkylation system is the further loss of a hydride from
a carbonium ion to form an olefinic intermediate; specifically

\[ C-C^+ + \text{HSO}_4^- \rightarrow C-C + \text{H}_{2}\text{SO}_4 \]
if dissociation of the ester is important.

The Schmerling Theory of Alkylation

The following is a presentation of the Schmerling mechanism using the isobutane-propylene system as an example. The mechanism is based on the carbonium ion theory of reaction.

A. A propylene molecule within the acid phase reacts with the catalyst to form the propyl carbonium ion:

\[
C=\text{C} - C + H\text{SO}_4^- \rightarrow C_3^+ \text{C-(HSO}_4^-)\]

B. The secondary ion formed is not as stable as the potential tertiary butyl ion; thus, the following reaction occurs

\[
\text{C-C} + \text{C}^+\text{C-(HSO}_4^-) \rightarrow \text{C}^+\text{C-(HSO}_4^-) + \text{C-C-C}
\]

as the propyl ion abstracts a hydride ion from isobutane. The net driving force for this reaction is the greater stability of the tertiary-butyl carbonium ion as compared to the secondary-propyl-carbonium ion.

The above reactions constitute the initiation reaction for alkylation of isobutane with propylene. As such they proceed to only
a limited extent; since (as will be shown) once the tertiary-butyl-carbonium ion is formed, the primary reactions to form 2,3- and 2,4-dimethylpentane from the reaction of $C_4^+$ and $C_3^-$ will proceed with no further aid from reactions A and B. This is not the case, however, for certain reactions other than primary reactions as will be shown later.

C. An alternate initiation sequence may also apply (the associated $HSO_4^-$ will be shown only as needed):

\[
\begin{align*}
C-C=C & + C-C^+\rightarrow C-C^+\rightarrow C-C-C^+\rightarrow C-C-C-C-C-C-C
\end{align*}
\]

\[
\begin{align*}
C-C & + C-C-C-C^+\rightarrow C-C^+\rightarrow C-C-C-C-C-C-C
\end{align*}
\]

The same reasoning with respect to the primary alkylation reaction applies to these reactions also.

D. The primary reaction - the simplest stoichiometric reaction - involves: (1) reaction of propylene with the tertiary carbonium ion to give the secondary 2,2-dimethylpentyl ion

\[
\begin{align*}
C^- & + C-C^+\rightarrow C-C-C-C^+\rightarrow C-C-C-C-C-C
\end{align*}
\]

(2) a methide shift to form the tertiary 2,4 isomer

\[
\begin{align*}
C-C-C-C^+ & \rightarrow C-C^-C-C-C
\end{align*}
\]
or a hydride transfer to yield the tertiary 2, 3 isomer

\[
\text{C-C-C}^+ \text{-C} \xrightarrow{\sim \text{C}} \text{C-C}^+ \text{-C-C-C}
\]

and (3) then the abstraction of a hydride from isobutane by one of the tertiary ions to form the primary product and to regenerate the tertiary butyl ion.

\[
\text{C-C}^+ \text{-C-C-C-C} \xrightarrow{\text{C-C}} \text{C-C}^+ \text{-C-C-C}
\]

The overall reaction is

\[
\text{C}_3\text{H}_6 + \text{C}_4\text{H}_{10} \rightarrow \text{C}_7\text{H}_{16}
\]

E. There are many side reactions, chief among which is the self-alkylation step. Here the tertiary butyl ion forms isobutylene, via hydrogen transfer, and subsequently alkylates another tertiary butyl ion to form the tertiary 2, 2, 4-trimethylpentyl carbonium ion. In order to form the extra butyl ion required, the initiation reaction must occur.

\[
\text{C=C-C} + \text{H}_2\text{SO}_4 \rightarrow \text{C-C}^+ \text{-C} + \text{HSO}_4^-
\]

\[
\text{C-C} + \text{C-C}^+ \rightarrow \text{C-C}^+ + \text{C-C-C}
\]
The trimethylpentyl ions may undergo isomerization (mainly to the 2, 2, 3 and 2, 3, 4 isomers) before abstracting hydride ions from isobutane to yield the octane fraction.

The overall reaction is

$$C_3H_6 + 2C_4H_{10} \rightarrow C_8H_{18} + C_3H_8$$

F. Other side reactions in alkylation are generally referred to as "destructive alkylation." They are so named since further reactions of the primary intermediates (the dimethylpentyl ions) are involved.

Among these reactions are the various routes to form the decyl ion and its saturated counterpart decane. The most logical route is analogous to the reaction of the isobutyl carbonium ion.
with propylene - that of the tertiary-dimethylpentyl cation with propylene. This route is supported by the following facts. There should be relatively large quantities of each species present in the catalyst phase (as propylene is very soluble in $\text{H}_2\text{SO}_4$ and the dimethylpentanes are second in quantity to isobutane within the hydrocarbon phase). Also, this reaction involves the simplest stoichiometry of any route to form the $\text{C}_{10}$ species.

\[
\text{C-C-C}^+\text{-C-C} + \text{C=C-C} \rightarrow \text{C-C-C-C-C}^+\text{-C}
\]

The above ion will most likely rearrange (probably to a tetramethyl-hexyl ion) due to the fact it is secondary and/or reacts with isobutane to form the decane congener.

The overall reaction is

\[
\text{C}_4\text{H}_{10} + 2\text{C}_3\text{H}_6 \rightarrow \text{C}_{10}\text{H}_{22}
\]

Although the above scheme is not mentioned specifically by Schmerling and others, it is completely analogous to the alkylation of isoparaffins such as isobutane and isopentane with propylene as reported by Kennedy (16). Thus, as it is consistent with the Schmerling mechanism, it is included here.

Another route to decanes involves the reaction of a dimethyl-butyl ion (the formation of this ion, also a destructive alkylation
reaction, will be illustrated later in this section). The 2, 3-dimethylbutyl ion may lose a proton to form a 2, 3-dimethylbutene intermediate.

\[
\text{C}-\text{C}^+\text{C} - \text{C} + \text{HSO}_4^- \rightarrow \text{C}=\text{C}\text{C} - \text{C} + \text{H}_2\text{SO}_4
\]

This unsaturated can react with a tertiary-butyl carbonium ion to form a tertiary decyl ion.

\[
\text{C} - \text{C}^+ + \text{C}=\text{C}\text{C} - \text{C} \rightarrow \text{C}=\text{C}\text{C}^-\text{C}^+\text{C} - \text{C}
\]

This ion can react with isobutane to form the respective decane or rearrange to another isomer of the decyl ion and go to that decane or undergo scission.

Data (29) indicates that formation of the decyl ion via the dimethylbutyl ion is somewhat unlikely due to the relative inertness of 2, 3-dimethylbutane to alkylation with isobutane in the presence of tertiary butyl fluoride. Also, the concentration of the resulting hexyl unsaturated may be inferred to be quite low as compared to a heptyl ion or propylene, making this route of formation of decyl species much less probable than the former route.

A discussion of the above reactions should include the possibility of scission of the decyl ion. This scission in the isobutane-propylene system would most logically result in the formation of two pentyl species, as other types of splitting usually considered (29) would
result in formation of isobutyl or propyl species. Both of these are already present in relatively large quantities in this system and would be considered a rate driving force opposite to scission.

The overall scission reaction is understood to be preceded by a hydride and a methide shift;

\[
\text{C-C-C-C}^+ - \text{C-C} \rightarrow \text{C-C}^+ - \text{C-C-C-C}
\]

and then scission.

\[
\text{C-C}^+ - \text{C-C-C-C} \rightarrow \text{C-C}^+ - \text{C-C} + \text{C-C=C-C}
\]

Still another possible route for forming the various decyl species (ions and saturates) is the reaction of isopentene with the isopentyl ion.

\[
\text{C-C=C-C} + \text{C}^+ - \text{C-C} \rightarrow \text{C-C}^+ - \text{C-C-C-C-C-C}
\]

This is probably not a significant reaction as it involves the formation first of one of the reactants from the other and both would be in very small quantities compared to the reactants of the preceding route for decyl species formation (7). Also it has been reported (16) that the above reaction would have a strong tendency to proceed in the opposite direction as discussed previously. However, if the above
decyl ion undergoes rearrangement, the reaction may proceed (apparently when the feed isoparaffin is isopentane) and subsequent disproportionation occurs (16) (29).

\[
\text{C-C=}-\overset{\text{C}}{\text{-C}} + \text{C-C}^+\text{-C} \longrightarrow (\text{C}_{10}^+) \longrightarrow \text{C-C}^+ + \text{C-C}=\text{C-C-C}
\]

This reaction probably is insignificant in the alkylation of isobutane, as the large quantity of isobutane present in the reacting medium would cause this reaction to reverse.

Another important reaction in the category of destructive alkylation is the formation of isopentane and 2, 3-dimethylbutane. First, the dimethylpentyl ion undergoes hydrogen transfer yielding a dimethylpentene.

\[
\text{C-C-C}-\overset{\text{C}}{\text{-C}} + \text{HSO}_4^- \longrightarrow \text{C-C}=\text{C-C} + \text{H}_2\text{SO}_4
\]

Second, the unsaturated subsequently reacts with a tertiary butyl ion to form an undecyl ion which readily isomerizes.
Third, the large ion thus formed cracks into isopentene and the dimethylbutyl ion.

Fourth, the paraffins corresponding to the above olefin and ion are formed as follows:

\[
\begin{align*}
C\text{-C=C-C} + H_2SO_4 & \rightarrow C\text{-C=H} + HSO_4^- \\
C\text{-C=H} + C-C & \rightarrow C\text{-C=H} + \text{C=C} \\
\text{and} \\
C\text{-C=H} + C\text{-C} & \rightarrow C\text{-C=H} + \text{C=C}
\end{align*}
\]

The overall reaction is

\[
C_3H_6 + 2C_4H_{10} \rightarrow C_6H_{14} + C_5H_{12}
\]
There is another route to form the two products above in the isobutane-propylene scheme; however, an ethylene intermediate is involved, and since sulfuric acid is a "poor" catalyst for ethylene alkylation (31), this route is not a logical one.

Since isopentane and 2, 3- and 2, 4-dimethylpentane are formed during the hydrogen transfer reaction of isobutane in the presence of t-butyl fluoride and boron fluoride (29), the scission of the 2, 3, 4-trimethylpentyl ion to isopentene and the secondary propyl cation is a logical step.

\[
\begin{array}{c}
\text{C-C-C}^+\text{-C-} \\
\text{C} \quad \text{C} \quad \text{C} \\
\end{array} \rightarrow \begin{array}{c}
\text{C-C=CC} \\
\text{C} \\
\end{array} + \begin{array}{c}
\text{C-C}^+\text{-C} \\
\text{C} \\
\end{array}
\]

The extent of this reaction in the isobutane propylene system would be difficult, if not impossible, to determine since both products are generated to a large extent by reactions already shown. At any rate, the extent of this reaction is probably relatively small due to the presence of the products of the reaction in relatively large quantities, and there is little justification for considering it in the propylene-isobutane system. When n-butene is used as the feed olefin, this may be an important reaction.

Schmerling does not specifically mention the mechanism by which the nonyl (chiefly trimethylhexyl) species is formed in the propylene system. However, data exists (7) which indicates that a large amount of trimethylhexane is formed in the alkylation of
isobutane with isopentenes, all isomers of which are probably present in isobutane-propylene alkylation. The reaction is probably

\[
\begin{align*}
\text{C-C-C}=\text{C} + \text{C-C}^+ & \rightarrow \text{C-C-C}^+-\text{C-C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C}
\end{align*}
\]

with the ion subsequently undergoing a hydride shift, then reacting with isobutane to form the saturate. This reaction is consistent with the Schmerling mechanism.

Another possible route would be the combination of the 2, 3-dimethylbutyl ion with propylene.

\[
\begin{align*}
\text{C-C-C}^+-\text{C} + \text{C} & \rightarrow \text{C-C-C}^+-\text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C}
\end{align*}
\]

The predominance of one over the other would be difficult to determine from experimental data as both the C_5 and C_6 species are largely formed by the same reaction and only the difference in their molar concentrations as saturated species would give any clue. This difference is generally small enough as to imply both reactions proceed to about the same extent. However, 2,2,5-trimethylhexane usually makes up more than 50% of the nonanes. Thus, the former is the most plausible reaction.

The overall reaction for the isopentene scheme would be

\[
3\text{C}_4\text{H}_{10} + 2\text{C}_3\text{H}_6 \rightarrow \text{C}_6\text{H}_{14} + \text{C}_9\text{H}_{20} + \text{C}_3\text{H}_8
\]
Note that in this case propane is formed, implying that the initiation reaction must proceed to supply one of the tertiary-butyl carbonium ions.

That for the dimethylbutyl ion scheme would be

\[ 2C_4H_{10} + 2C_3H_6 \rightarrow C_5H_{12} + C_9H_{20} \]

Since no propane is formed by this scheme, it is possible that a measurement of the yield of propane would be a way to infer how much nonane is formed by what reaction. However, the nonane formation is small as compared to octane formation in this system - another propane producer. There would be a problem with accuracy in using the propane formed as a means of determining the proper reactions. In many cases the determination of propane in such a sample of alkylate would be subject to enough error to disguise the small amount formed via any nonane formation.*

**Other Mechanism Studies**

While the Schmerling mechanism has enjoyed much popularity and much research has been based on it, there are problems which some feel that it does not adequately explain. In his theory, Schmerling implies that all octanes are formed via the same general reaction when propylene is used even though the formation of the

---

* The standard method of analysis of such a mixture utilizes a capillary-column equipped, temperature-programmed gas chromatograph. The thin, sharp peak from a low boiler such as propane is the source of much error in determining this component's relative weight percent.
trimethylpentanes is the most logical. When butenes are used, it is assumed that dimethylhexanes arise from direct alkylation of butene-1 (13). This assumes that butene-1 is present regardless of whether butene-1 or butene-2 is fed to the rapid isomerization and subsequent equilibrium between butene-1 and butene-2. However, experiments carried out by Zimmerman, Kelly, and Dean (33) pointed out that this source of dimethylhexane would not be present when isobutylene is used as the only feed olefin and yet 15.2% of the observed octanes consisted of dimethylhexanes. This is to be compared with 15.3% for butene-1 and 11.6% for butene-2. The authors explained this by postulating the isomerization of the trimethylpentyl ion to the dimethylhexyl ion which would subsequently form dimethylhexanes.

Hofmann and Schriesheim (11) also used the three butene isomers to alkylate isobutane. One of their goals was to determine the sources of dimethylhexanes. Carbon 14 tagged olefins were used, and the relative specific activity of the products were analyzed. When using isobutylene the activity of the dimethylhexane fraction was found to be triple that of the trimethylpentanes. The relative specific activity of the dimethylhexanes when butene-1 was used was found to be about half again as great as the trimethylpentanes. The authors concluded from these results: (1) Self alkylation of isobutane is significant even when the olefin is a butene - the general reaction being

\[ C_nH_{2n} + iC_4H_{10} \rightarrow C_nH_{2n+2} + iC_4H_8 \]
and (2) the formation of dimethylhexanes must be partially due to
dimerization of isobutylene (either in the feed stream or formed via
the reaction above) via an allylic ion.

\[ \text{iC}_4 \text{H}_8 + \text{iC}_4 \text{H}_{10} \rightarrow \text{iC}_8 \text{H}_{18} \]

An earlier paper (10) by the authors showed the source of the allylic
ion to be

\[ \text{iC}_n \text{H}^{+} + \text{iC}_4 \text{H}_8 \rightarrow \text{iC}_n \text{H}_{n+2} + \text{iC}_4 \text{H}^{+} \]

They stated that 2,5-dimethylhexadiene-1,5, the precursor of the C\(_8\)
ion above, can be saturated to a dimethylhexane via hydrogen transfer.
These reactions were not shown, but presumably they occur as
follows:

\[ \text{C} = \text{C} - \text{C} - \text{C}^{\dagger} - \text{C} + \text{C} - \text{C} \rightarrow \text{C} = \text{C} - \text{C} - \text{C} - \text{C} + \text{C} - \text{C} - \text{C} \]

\[ \text{C} = \text{C} - \text{C} - \text{C} - \text{C} + \text{H}^{+} \rightarrow \text{C}^{\dagger} - \text{C} - \text{C} - \text{C} - \text{C} \]

\[ \text{C} - \text{C}^{\dagger} - \text{C} - \text{C} - \text{C} - \text{C} + \text{C} - \text{C} - \text{C} \rightarrow \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} + \text{C} - \text{C} - \text{C} \]
Thus, a reasonable route for the formation of a dimethylhexane is through the combination of isobutylene with its ionic counterpart, the allylic ion and subsequent saturation.

Kennedy (16) used data obtained from the isomerization of dimethylpentanes promoted by isopropyl fluoride - boron trifluoride to present a rather unique route of formation of dimethylhexanes. When either the 2,3 or 2,4 isomer was used, a relatively significant part of the product was octanes and hexanes. Of the octanes, only dimethylhexanes were present; of the hexanes, the methylpentanes were the largest fraction. Kennedy postulated that in a system containing dimethylpentyl cations (such as in the alkylation of isobutane with propylene) the following reactions might occur:

\[
\begin{align*}
\text{C-C-C-C}^+\text{-C} & \rightarrow \text{C-C-C=C-C} + \text{H}^+ \\
\text{C-C-C-C}^+\text{-C} + \text{C-C-C=C-C} & \rightarrow \text{C}_{14}^+ \\
\text{C}_{14}^+ & \rightarrow \text{C-C-C-C=C-C} + \text{C-C-C}^+\text{-C} \\
\text{(or C-C}^+\text{-C-C-C)}
\end{align*}
\]
The exact isomers formed would be dependent upon the extent of the isomerization of the \( C_{14} \) ion.

The overall reaction if this were to occur in the isobutane-propylene system would be

\[
2C_3H_6 + 2C_4H_{10} \rightarrow C_6H_{14} + C_8H_{18}
\]

A more recent work by Mosby (23) involving alkylation of iso-butane with butene-1 at various retention times with a range of 15 to 60 seconds shows the yields of dimethylhexanes and trimethylpentanes do not vary in the same manner with retention time. This indicates that, for butene-1 at least, the dimethylhexanes are not formed by isomerization of trimethylpentyl ions. Rather the data supports Iverson and Schmerling's (13) conclusions that the direct alkylation of butene-1 is the chief source of the dimethylhexane, i.e.,

\[
\begin{align*}
C & \quad C \quad C \\
C-C^+ + C=C-C-C & \quad \rightarrow \quad C-C-C-C-C^+\quad C-C
\end{align*}
\]

No conclusions were drawn, however, concerning the other two olefin isomers with respect to dimethylhexane formation.

Another conclusion drawn from this work was that nonanes appear to be products of the reaction of isopentane and the feed butenes in an analogous manner to the alkylation of isobutane to form octanes. This again may be a conclusion only valid for butene
alkylation. In the case of propylene alkylation there is the large possibility that the isopentene intermediates formed react with isobutane to form nonanes.

Both the work of Hofmann and Schriesheim (11) and that of Mosby and Albright (24) indicate that the lighter fractions ($C_5$, $C_6$ and $C_7$) alkylate obtained in isobutane-butene alkylation result from cracking of a $C_{12}^+$ ion. This does agree with the Schmerling hypothesis of formation of pentanes and hexanes via a $C_{11}$ ion in isobutane-propylene alkylation. A point of difference here is that at least some of the $C_{12}^+$ was considered to be the butene trimer. Whereas Schmerling considered the $C_{11}$ ion a result of further reaction of $C_7$ intermediates with isobutane. This latter would imply the $C_{12}$ ion arises from further reaction of $C_8$ intermediates rather than polymerization. It probably is the case that polymerization is more of a factor in light product formation in the case of butene than in the case of propene where the trimer would be a $C_9$ species. The reason is that scission of this species would either form isobutane or normal butane together with isopentane. The isobutane is unlikely due to the already high concentration of this species present, and the normal butane because of the absence of this compound in propylene-isobutane alkylate products (7).

Another problem not adequately explained by the Schmerling mechanism is comparatively large variations of the composition of the alkylate over a small range of acid concentration. The size of
the effects - a decrease in two octane numbers for a decrease in acid concentration of from 95% to 89% by wt. (7) does not seem to be readily explained by the rather simple reaction of the olefin and acid as shown in the Schmerling sequence. Even less explicable by this theory is the fact that product quality is better at an acid concentration of 95-96% than at either higher or lower strengths (7). Cupit, Gwyn and Jernigan clarify the situation somewhat by speaking of "overall" catalyst activity which includes "(1) its ability to produce carbonium ions via proton transfer to olefinic molecules and (2) its solubility for isobutane, since formation of saturated product occurs via hydride-ion transfer from isobutane to alkylate range carbonium ions." (7) The ability of the acid to protonate an olefin should be proportional to the strength of the acid; however, isobutane solubility is increased as the acid is organically diluted. This would explain the fact that the optimum acid concentration is not the highest concentration (excluding "fuming" acid).

Hofmann and Schriesheim concluded that the organic diluents themselves could (1) aid in isobutane solubility and/or (2) act as intermediates in hydride transfer reactions - either action would have the same net effect of allowing "alkylation to occur between isobutane and the olefin." The authors contacted an acid sludge with isobutane and obtained a product which indicated (to them) that the hydride transfer function of the diluent was most important. Mosby (23) on the
other hand, felt that the solubility of isobutane effect is more important since his data indicated higher acid strengths gave higher rates of hydride transfer from isobutane.

Schmerling's theory indicates that the carbonium ions themselves act as intermediates, implying the anions and cations remain more or less disassociated much as an inorganic salt in solution. Also, the general conception has been that conditions which allow stable olefin esters (completely associated anion and cation as opposed to a salt-in-solution effect) to form lead to a much degraded product (7) (4). This idea has lent much support to Schmerling's ionic mechanism. Shlegeris (30, 31) however, cites three Texaco patents which indicate that under the proper conditions dipropyl esters formed by reacting propylene with spent alkylate acid could be contacted with isobutane and alkylate and regenerated sulfuric acid obtained. His data from a small, five-stage reactor showed the presence of olefin polymerization products at low retention times which he concluded to be intermediates to alkylate formation. Noting also that Naworski (25) obtained very high reaction rates for the polymerization of butene-1 in sulfuric acid, he has proposed a slightly different general mechanism than Schmerling's. Assuming conditions which minimize high local concentrations of olefin, it is:

1) \( \text{H}_2\text{SO}_4 + \text{Olefin} \rightarrow \text{Ester} \)

2) \( \text{Ester} + \text{Isobutane} \rightarrow \text{Primary Alkylate} \)
This scheme, however, does not rule out carbonium ions as intermediates; it may serve, however, to show that the formation of the carbonium ion by the reaction

\[ \text{Ester} \rightarrow \text{Carbonium Ion} + \text{Anion} \]

may indeed be rate limiting in alkylation as Bethell and Gold suggest for reactions involving carbonium ions in general.

**Kinetics**

Because of the physical problems involved with alkylation the development of a detailed kinetic model is yet to be included in research on this system. One work in the area of kinetics and mass transfer exists, but the chemistry assumed has been simplified to the point of including only "C_8" and "other alkylate" to obtain a model. The work was performed by Jernigan, Gwyn, and Claridge (14) and has served to point up the mass transfer limitations which exist in alkylation.

Five general reactions were assumed:

1. \[ C_{n_1}H_{2n_1} + H^+ \rightarrow k_1 C_{n_1}H_{2n_1}^+ \]
2. \[ C_{n_2}H_{2n_2+1} + iC_4 \rightarrow k_2 C_{n_2}H_{2n_2+2} + iC_4^+ \]
3. \[ C_{n_1}H_{2n+1} + C_{n_2}H_{2n_2+1} \rightarrow k_3 C_{n_3}H_{2n_3+1} \]
4. \[ C_{n_3}H_{2n_3+1} \rightarrow k_4 C_{n_3}H_{2n_3} + H^+ \]
5. \[ C_{n_3}H_{2n_3+1} \rightarrow k_5 C_{x}H_{2x} + C_{y}H_{2y+1}^+ \]

No discrimination was made between a secondary-butyl or tertiary-butyl cation reacting with butene and presumably they assumed \( k_i \)
would be the same for either case. Also the size of the olefin or paraffin was not a parameter - i.e., \( n \) may take on several values for each of the above reactions.

A further assumption made was that "all alkylate is produced via C\(_8\) carbonium ions." This may be summarized using equations 2, 3 and 5 above with values of \( n_1=4, n_2=8, \) and \( n_3=12. \)

\[
\begin{align*}
6. & \quad C_8H_{17}^+ + IC_4H_{10} \xrightarrow{k_2} C_8H_{18} + C_4H_9^+ \\
7. & \quad C_8H_{17}^+ + C_4H_8 \xrightarrow{k_3} C_{12}H_{25}^+ \\
8. & \quad C_{12}H_{25}^+ \xrightarrow{k_5} \text{other alkylate}
\end{align*}
\]

Assuming an ideally mixed reactor at steady state, the following rate equations were written:

1) The overall rate of depletion of the olefin was found using equations (1) and (2).

\[
\frac{d}{dt}[C_4H_8] = k_1[C_4H_8] + k_3[C_4H_8][C_nH_{2n+1}] \quad \text{a)}
\]

where the olefin reaction rate, \( r_{C_4H_8} \), was computed as the olefin feed rate per unit volume of acid in the reactor and \([C_nH_{2n+1}]\) is the total concentration of all the carbonium ions within the catalyst.

2) The production and consumption of carbonium ions were set equal using reactions (1) and (4).

\[
k_1[C_4H_8] = k_4[C_nH_{2n+1}] \quad \text{or} \quad [C_nH_{2n+1}] = \frac{k_1[C_4H_8]}{k_4} \quad \text{b)}
\]
3) The substitution of the expression for $[C_{n}H_{2n+1}]$ was made in the olefin balance to give:

$$r_{C_{4}H_{8}} = k_{1}[C_{4}H_{8}] + \frac{k_{3}k_{1}}{k_{4}} [C_{4}H_{8}]^{2}$$  \hspace{1cm} (c)

4) At steady state the total number of ions in the reaction medium could be considered constant, and they interpreted $k_{1}[C_{4}H_{8}]$ to be equal to the rate of polymer formation. This was assumed negligible with respect to the alkylate formation which is represented by $\frac{k_{3}k_{1}}{k_{4}} [C_{4}H_{8}]^{2}$. The previous equation simplifies to:

$$r_{C_{4}H_{8}} = \frac{k_{3}k_{1}[C_{4}H_{8}]^{2}}{k_{4}}$$  \hspace{1cm} (d)

and rearranging gives the olefin concentration in the catalyst phase.

$$[C_{4}H_{8}] = \sqrt[3]{\frac{k_{4}r_{C_{4}H_{8}}}{k_{1}k_{3}}}$$  \hspace{1cm} (e)

5) The rate of mass transfer of isobutane into the acid phase was set equal to its consumption by chemical reaction.

$$k_{m}A K_{b} [iC_{4}H_{10}]_{HC} - [iC_{4}H_{10}] = k_{3}[iC_{4}H_{10}] \left( [C_{n}H_{2n+1}]^{+} - [iC_{4}H_{9}^{+}] \right)$$  \hspace{1cm} (f)

where $[iC_{4}H_{10}]_{HC} = \text{concentration of isobutane in the hydrocarbon phase}$
\[
\left[ C_nH_{2n+1}^+ \right] = \text{total carbonium ions in the system}
\]

\( k_m \) = isobutane mass transfer coefficient

\( A \) = isobutane mass transfer area per unit volume of acid

\( K_b \) = distribution coefficient of isobutane between phases

Solving the above equation for the isobutane concentration in the acid phase gives

\[
\left[ iC_4H_{10} \right] = \frac{K_b [iC_4H_{10}]_{HC}}{1 + \frac{k_2}{k_mA} \left( \left[ C_nH_{2n+1}^+ \right] - [iC_4H_9^+] \right)}
\]

6) The reaction rates of \( C_8 \) and "other alkylate" were solved for using equations 6, 7, and 8:

Equation 6:

\[
[r_{C_8} = k_2 \left[ C_8H_{17}^+ \right] [iC_4H_{10}]]
\]

Equations 7 and 8 were combined (assuming evidently - the authors did not explicitly say so - that \( C_{12}H_{25}^+ \) was the sole route of formation for all other alkylate), \( C_{12}H_{25}^+ \) was eliminated, and \( k_3 \) and \( k_5 \) were combined but still termed \( k_3 \):

\[
[r_{\text{other alkylate}} = k_3 \left[ C_8H_{17}^+ \right] [C_4H_8]]
\]

and dividing the rate equation from reaction (6) by the
rate equation for reactions (7) and (8) gives

$$\frac{r_{C_8}}{r_{\text{other alkylate}}} = \frac{k_2[iC_4H_{10}]}{k_3[C_4H_8]}$$

Substituting for $[iC_4H_{10}]$ and $[C_4H_8]$, noting that by equation (f)

$$\left( [C_nH_{2n+1}^+] - [iC_4H_9^+] \right) = k_1 [C_nH_{2n+1}^+]$$

where $k_1$ is the fraction of carbonium ions which are not $C_4$ carbonium ions

$$\frac{r_{C_8}}{r_{\text{other alkylate}}} = \frac{k_2[iC_4H_{10}]}{\sqrt{F \cdot C_4H_8} + \frac{k_2K_1F}{k_mAK_b}C_4H_8} = k_rQ$$

where $k_r = \frac{k_2K_b}{k_3k_4} \frac{1}{k_1}$

and $Q$ is defined as an overall severity parameter.

A severity factor $J$ was defined

$$J = \frac{[iC_4H_{10}]_{HC}}{\sqrt{F \cdot C_4H_8}}$$

and substituting for $[iC_4H_{10}]$ in the previous equation and rearranging
\[
\frac{J}{r_{C_8}/r_{\text{other alkylate}}} = \frac{1}{k_r} + \frac{K_l}{k_m C K_b} \sqrt{\frac{r_{C_4H_8}}{m}}
\]

Cupit et al. (7) used the correlation for the mean drop diameter calculated by the methods of Handlos and Baron, Kolmogoroff, and Langlois to obtain the mass transfer area. This is

\[
A = C \left( \frac{(H_e)(H)}{(H_e)(H) + V} \right)
\]

where

\( C \) = constant of proportionality

\( V \) = volume fraction of acid in the system

\( H \) = volume fraction of hydrocarbon in the system

\( H_e \) = volume fraction of total hydrocarbon that is emulsified

Thus

\[
\frac{J}{r_{C_8}/r_{\text{other alkylate}}} = \frac{1}{k_r} + \frac{K_l}{k_m C K_b} \cdot \frac{\sqrt{r_{C_4H_8}[(H_e)(H) + V]}}{(H_e)(H)}
\]

\[
= \frac{1}{k_r} + \frac{K_l}{k_m C K_b} \cdot G
\]

A plot of \( J \) factor vs. \( G \) yields \( 1/k_r \) and \( K_l/(k_m C K_b) \).

The values were 34.9 for \( 1/k_r \) and 33.9 for \( K_l/k_m C K_b \).

Various values for \( Q \) were calculated using equation (k) in the form

\[
Q = \frac{r_{C_8}}{r_{\text{other alkylate}}}/k_r
\]
The use of the correlations obtained lie in the parameter Q. Both alkylate quality ($r_{C_8}/r_{other alkylate}$) and octane number were found to be related to Q by the general linear relation

\[ y = mQ + b \]

where \( y \) is the independent variable in question, \( m \) is the slope of the plot, and \( b \) is the intercept. The value for \( m \) in both cases was positive. Also, the increase of the \( C_6 \) through \( C_{11} \) yield and decrease of the \( C_{12}^+ \) yield were both found to be approximately linear functions of Q on a log-log plot.

In obtaining the final results (numerical), a detailed characterization of the emulsion (including emulsion settling curves to obtain the volume of hydrocarbon emulsified per volume of stable emulsion and the volume of acid in the reactor) had to be performed. This was a necessity as the alkylate quality ratio was found to be a strong function of the percent acid in emulsion. Then, too, the hydrocarbon was not 100% emulsified until the acid in the emulsion reached at least 48%. At this point the authors stated that mass transfer area (assuming approximate ideal mixing) became maximum. Alkylate quality, however, tended to peak at a value of 60% acid in emulsion due to "opposing effects of the decreasing space velocity and decreasing mass transfer area."

It would appear, therefore, that such emulsion characterization would be unnecessary if the following conditions were met:
1. The hydrocarbon must be 100% emulsified.

2. The acid in emulsion should be about 60% by volume.

3. The agitation should be such that ideal mixing is approximated.

As it does correlate well the alkylate quality and performance number with the group known as the severity parameter, this type of model is particularly suited to predict process operations. It does not, however, give more than a little insight to the true kinetics of the alkylation reactions due to the gross chemistry assumed. The model does point out that mass transfer limitations do exist for isobutane transfer into the acid phase. However, the extent of this limitation can only be determined qualitatively with severity of operation, as it is not separable mathematically from reaction rate effects.

Another work, performed by Naworski (25), is a study of the kinetics of butene-1 polymerization in sulfuric acid. Though not directly related to alkylation systems, it is applicable since this is considered to be a competing reaction under less than ideal conditions. Using a capillary flow reactor, he found a first order rate constant (assuming first order kinetics) of from 1.7 to $13.8 \times 10^4$ sec.$^{-1}$ at 25°C. depending on the value of the diffusivity he calculated from the Wilke-Chang equation. It is interesting to note that these values were 15% lower than those he found at 17.5°C. He does not explain this anomaly, however.
He was forced (from the lack of available data) to use a single, temperature-independent value for the solubility of butene-1 in sulfuric acid for the calculation of the rate constants. He assumed this value to equal the value of isobutane at 56°C. The fact that butene is probably far more soluble than this would indicate that his reported values could be off by more than the order of magnitude of accuracy he claimed. Regardless of this, the work shows the polymerization reaction to be rapid. It quantitatively confirms the need for minimizing olefin concentrations in alkylation.

Also, along the same lines Shlegeris has proposed the formation of alkylate via esters formed by the action of the acid on the olefin; however, he proposes that too high a concentration of olefin suppresses this reaction in favor of polymerization.

Operating Variables

Research on the optimization of process variables to obtain higher qualities of alkylate - i.e., to maximize the primary reaction product - dates back to the initial stages of commercial use in the late 1930's. The works of Birch et al. (4), McAllister et al. (21) and Ipatieff and Pines (12) are examples of this early work. However, this last research is only related to alkylation.

Birch et al. alkylated various olefins under varying reaction conditions. A significant observation was made regarding the sulfuric acid catalyzed isobutane-propylene alkylation. When the reaction was attempted at 20°C using 97% sulfuric acid, only isopropyl...
hydrogen sulfate and the corresponding polymers were formed. Using 101.7% acid at this temperature, however, they obtained alkylation - 90% of the debutanized product boiled below 150°C. (the boiling point of normal nonane being 150.5°C.).

McAllister and co-workers obtained a product consisting of about 70% dimethylpentanes when alkylating isobutane with propylene at 30°C. using a sulfuric acid catalyst of 98%. This work was primarily concerned with obtaining a reaction mechanism through reaction of various olefins with isobutane; however, one of the by-products of the work was the reporting of good operating temperatures and catalyst concentrations.

Ipatieff and Pines varied the temperature and quantity and strength of sulfuric acid in experiments involving the polymerization of olefins in sulfuric acid. Of special significance to alkylation was the fact that the yield of paraffinic hydrocarbons decreased considerably with the decrease in sulfuric acid concentration. In fact, with a concentration of less than 87% no paraffinic hydrocarbons were formed. This would imply that acid concentrations below around 87% would also give high amounts of unsaturates in alkylation, degrading product quality.

Work in this area since is voluminous. Variables of interest have been variations of olefin and isoparaffin; catalyst activities, composition, and physical properties; acid strength and consumption; temperature; isoparaffin to olefin ratios; olefin space
velocities; and the degree of mixing and mass transfer (7). Cupit, Gwyn, and Jernigan (7); Jones (15); Putney (27); and Schmerling (29) all present a good summary of the results of the research in this area. As might be expected most of this work in alkylation is concerned with isobutane-butene alkylation. However, of late there has been an increasing interest in propylene alkylation; and, therefore, increasingly more effort has been put into the investigation of this process (11, 17).

Propylene alkylation proposes several problems. Propylene forms stronger bonds with sulfuric acid (and hydrofluoric) than do the butene isomers (7); therefore, generally higher temperatures and acidities appear to be needed for alkylation. In reacting pure propylene with isobutane it has been difficult to obtain a satisfactory alkylate as to low end points, performance numbers, etc. Butenes have been shown to act as good promoters of propylene alkylation (7, 33). Acid consumption (lb. acid degraded/gal. alkylate produced) is reported by Cupit and co-authors (7) to be 2 1/2 to 3 times higher for propylene than for isobutane under the same conditions.

One work which has sought to solve these problems on a commercial scale is that of Knoble and Hebert (17). The commercial unit which they report their results from was initially fed with 100% propylene for the olefin. However, this caused rapid sulfuric acid depletion - from 99.5 to 82.5% in the first 30 hours of operation. A ratio of 65/35 by volume of propylene to butene was then substituted
resulting in yields of good alkylate (F-1 - 3 cc. octane numbers equal to 100 plus, and acid consumption less than 2 pounds per gallon of alkylate). This alkylate, however, had an end point of 430°F. and a 400°F. end point was desired. Therefore, other variables, including temperature, external isobutane to olefin ratio, acid concentration, percent propylene in the olefin, impeller speed, and percent acid in the emulsion were investigated.

Over the ranges of variables investigated - 8/1 to 15/1 isobutane to olefin, 96 to 85 weight percent acid, 40 to 65°F., 510 to 620 rpm on impeller speed, 50 to 70 percent propylene in olefin, and 50 to 65 percent acid in emulsion - the largest improvement occurred when the impeller speed was raised to 620 rpm and the percent of acid in emulsion was raised to 65%. This indicated that adequate mass transfer is even more critical with propylene than with butene alkylation.

Knoble and Hebert were able to draw several conclusions from this work:

1. Propylene concentrations of 95% and greater (with respect to the total olefin in the feed) may be successfully alkylated in a sulfuric acid catalyst. The product obtained typically may have high octane numbers and less than 400°F. end points, and the acid assumption may be decreased by about one-half.

2. "The key to successful alkylation of propylene is a highly dispersed reactor emulsion, which results primarily from the
control of two variables - the degree of mixing and the percentage acid in the reactor."

3. The other alkylation conditions (temperature, isobutane to olefin ratio, and acid strength) are about the same as those for butene. Here the authors presuppose that pure propylene is not being alkylated.

4. Greater power for mixing is required for propylene than for butene.

The above work, while fairly extensive, leaves one main question unanswered - under what conditions may propylene as the sole olefin be alkylated with isobutane in sulfuric acid and have the primary reactions of formation of isoheptanes predominate? Also, what are the quantitative effects of variations in these conditions on the primary and secondary reactions? Obviously more research is needed in this area of alkylation.

One of the most recent attempts at correlating operating variables with product quality is the work of Shlegeris and Albright (31) for propylene and butylene alkylation. In addition to the mechanism studies, correlations were made using a least squares analysis of data on the effect on product distributions by the variables of feed, acid strength, agitator speed, retention time, and variation of the C4 olefin. More important to this work were the results obtained using 99% pure propylene as the olefin feed - over a temperature range from 10°C to 40°C. The resultant yield was higher and of a
higher quality (the percent heptanes reached a maximum at 25°C and then decreased; however, the heavy ends decreased continually).

Increasing the agitator speed from 600 to 3,000 rpm produced even a more marked increase in product quality, and yields of product were higher with higher acid strength. It appears again that one of the most important factors in alkylation of propylene is the degree of mixing.

Shlegeris and Albright do answer some important questions about effects of operating variables on alkylation. They also establish that primary alkylation reactions are extremely fast (residence times were from 5 to 60 seconds in obtaining good yields), but that most of the product may be due to the slower secondary reactions. No attempt to calculate the rate constants was made, however.

**Mixing and Mass Transfer in Liquid-Liquid Heterogeneous Reaction Systems**

An important part of the analysis of the alkylation reactions is to determine the relation between mass transfer and the true rates of reaction. Generally, only the overall rates of mass transfer may be evaluated as the amounts of hydrocarbon in the acid phase are not readily determinable. The overall rate of mass transfer for a component may be found by making a material balance on this component in the hydrocarbon phase:

\[
\text{Moles } C_i \text{ in } - \text{ moles } C_i \text{ out } = \text{ consumption of } C_i \text{ by reaction} = \text{ rate of mass transfer of } C_i \text{ into the acid phase}
\]
Mathematically, the rate of mass transfer may be stated

$$N_i = k_{m_i}A\left([C_i]_{HC}K_{D_i} - [C_i]_{acid}\right)$$

where $N_i$ = overall rate of mass transfer between phases of component $i$

$k_{m_i}$ = mass transfer coefficient of component $i$ through the acid

$A$ = area of mass transfer

$K_{D_i}$ = distribution coefficient of component $i$ between hydrocarbon and acid phases

$[ ]$ = concentration

$HC, acid$ = subscripts indicating hydrocarbon and acid phases

The problem is, of course, that the only "knowns" in the equation are $N_i$ and $[C_i]_{HC}$. However, $k_{m_i}$, $A$, and $[C_i]_{acid}$ are the most important variables which affect the product distribution.

In the work of Jernigan et al. (14) an evaluation of a group of parameters was made as discussed in the previous section. This included the product $k_{m_i}AK_{D_i}$. However, $k_{m_i}$ and $K_{D_i}$ must be determined individually to evaluate $[C_i]_{acid}$. This is not possible with the model obtained by the author.

In general, the evaluation of the mass transfer terms $k_{m_i}$, $A$, etc., in liquid-liquid systems has been carried out in non-reacting systems (32)(19). In this type of experimental work the values of concentrations in both phases have been evaluated. Also, the area of mass transfer has been studied visually (32).
As a general rule most discussions of liquid-liquid mass transfer (with or without reaction) are largely theoretical (5). Experimental measurements which apply to a system such as alkylation are all but absent from the literature as conventional means of bubble size determinations, concentration determinations, etc., are inapplicable.

As a result, the best that can be done is to approximate the system with a nonreacting system with similar physical properties. Malloy and Taylor (19) have done this type of work with a system which has approximated alkylation conditions. They used a horizontal, cylindrical continuous stirred tank. Heavy alkylate (boiling from 300 to 450°F.) was used as the dispersed feed, and a 51% by volume solution of corn syrup was used as the continuous phase. (The physical properties actually approximated those of an aluminum halide-hydrocarbon system rather than a sulfuric acid - hydrocarbon system. The only principle difference, however, is the greater viscosity of the sulfuric acid. This would cause the mass transfer coefficients reported in this work to be higher than expected from a sulfuric acid system.)

The diameter of the vessel was 7.5 inches. The ratios of the diameter of the turbine and the emulsion depth to the reactor diameter were 0.35 and 0.81 respectively. The reactor was 14% baffled, and the turbine was located 1.1 times its own diameter from the bottom of the reactor.
Acetic acid was contained in the alkylate and was transferred to the syrup solution. By measuring the overall rate of transfer of acetic acid and its concentration in both phases (by titration) within the reactor, the mass transfer coefficient could be calculated:

\[ N = K_a V(C_p - K_D C_w) \]

where

- \( N \) = mass transfer rate of acetic acid
- \( C_p \) = concentration of acetic acid into dispersed phase
- \( C_w \) = concentration of acetic acid in the continuous phase
- \( K_D \) = distribution coefficient of acetic acid between phases
- \( K \) = overall mass transfer coefficient
- \( a \) = interfacial area per unit volume of emulsion bed
- \( V \) = volume of bed

The resulting mass transfer coefficient with a "very small" drop size was

\[ K_a = 220 \text{ lb. HOAc} \left( \frac{\text{lb. HOAc}}{\text{hr.(ft.}^3\text{ bed)}} \right) \frac{\text{lb. feed}}{\text{lb. feed}} \]

This value was obtained with a dispersed phase volume of 8% of the emulsion volume. In a separate series of tests using the same reaction the authors noted an increase in the volume percent of the dispersed phase by a factor of 2.6 effected an increase in the mass transfer coefficient by a factor of 3 - about a one-to-one correspondence.
In another test water was substituted for the corn syrup solution as the continuous phase. The viscosity of the syrup solution was about ten times that of the water; however, the resulting mass transfer coefficient with water (with all other physical conditions being equal) was only 2.1 times greater than that of the corn syrup solution.

The level of power used for these tests was in the range of 0.11 to 0.18 hp/(k x 1,000 gal.). The factor k is the power number as defined by Rushton, Costich, and Everett (28) and was approximately equal to 6.3.

**Summary**

Research in the area of alkylating isobutane with olefins has centered around the isobutane-butene-sulfuric acid system. However, using propylene as the olefin has been increasingly investigated as of late.

The primary objects of the research to date have been the elucidation of the mechanism of alkylation and the effects of operating variables on product quality. Two works on kinetics have been made; however, one involves alkylation only indirectly and the other - that of Jernigan, Gwyn, and Claridge - involved a rather over-simplified chemistry. It was in reality a sophisticated study of operating variables on product quality.

What is totally lacking is a kinetic study based on the individual rates of production of each of the products of both the
primary and secondary reactions. Such a study, however, can only be made with the knowledge of the results of prior work such as reported in this chapter; thus, it is recognized that the necessity of "first things first" - the mechanism and conditions of reaction must be well defined before a kinetic study may be attempted - has contributed to putting off this type of work. It is felt now that the state of the art has advanced to the point where a valid measurement of the reaction kinetics may be made. To be sure, the same problems of defining the concentrations of reactants still exist, but it is felt that this problem may be overcome by extrapolation of present knowledge.

Further, it is felt that such a study should be made on the propylene-isobutane-sulfuric acid system. Not only will the information derived from this be applicable to the butene system, but further general knowledge on alkylating propylene will be gained in the process as opposed to considering the well-studied butene-isobutane-sulfuric acid system.

IV. Statement of the Problem

A detailed analysis of the kinetics of the alkylation of isobutane with propylene using a sulfuric acid catalyst is needed. The object of the study is to obtain the rate constants as a function of temperature for the various reactions which produce major and minor products. In addition, the qualitative effect of catalyst concentration at various temperatures will also be determined.

Such a study will be implemented by an experimental program based
on data obtained from a pilot scale, stirred tank reactor with a perfectly mixed hydrocarbon phase to minimize mass transfer resistance.

The value of such a study, it is hoped, will be in making olefin-isobutane alkylation more of a science rather than an art. Also, this will be one of the few liquid-liquid, heterogeneous, complex reaction studies to be made, and hopefully new ideas will be gained which will be useful in subsequent research of this type.
I. Introduction

The Schmerling mechanism has been selected as the basis of the kinetic model for the alkylation of isobutane with propylene. As can be seen from Chapter I, this is the best overall theory of alkylation reactions. All other theories since this one are generally extensions of it. This theory will be used with some modifications in light of what are considered to be the most valid extensions from recent work.

On the basis of the modified mechanism to be presented, the reactions which will be considered for the foundation of the kinetic model are presented in the following tables. The symbol X\(^{-}\) will be used for HSO\(_4\)\(^{-}\), and C\(_n\)\(^+\)X\(^{-}\) will be used to denote carbonium ions with the corresponding anion in solution. The numbers for the reaction rate constants bear no relation to the table in which the reaction appears.

In Table 2-1.1 the initiation reactions are given. These reactions, in addition to their initiation function as has been shown, are the source of carbonium ions for the self-alkylation reactions.

In Table 2-1.2 the primary reactions are given. These reactions are the ones from which the dimethylpentanes are formed.
**TABLE 2-1.1**

*Initiation Reactions*

\[ C_3^= + HX \xrightarrow{k_1} C_3^+X^- \]  \hspace{1cm} (2-1.1)

\[ C_3^+X^- + iC_4 \xrightarrow{k_2} C_3 + iC_4^+X^- \]  \hspace{1cm} (2-1.2)

**TABLE 2-1.2**

*Primary Reactions*

\[ iC_4^+X^- + C_3^= \xrightarrow{k_{11}} iC_7^+X^- \]  \hspace{1cm} (2-1.3)

\[ iC_7^+X^- + iC_4 \xrightarrow{k_5} iC_7 + iC_4^+X^- \]  \hspace{1cm} (2-1.4)

**TABLE 2-1.3**

*Self-Alkylation Reactions*

\[ iC_4^+X^- \xrightarrow{k_9} iC_4^= + HX \]  \hspace{1cm} (2-1.5)

\[ iC_4^+X^- + iC_4 \xrightarrow{k_{10}} iC_8^+X^- \]  \hspace{1cm} (2-1.6)

\[ iC_8^+X^- + iC_4 \xrightarrow{k_6} iC_8 + iC_4^+X^- \]  \hspace{1cm} (2-1.7)
### TABLE 2-1.4

**Destructive Alkylation Reactions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$iC_7^+X^- \xrightarrow{k_{12}} iC_7^+ + HX$</td>
<td>2-1.8</td>
</tr>
<tr>
<td>$iC_7^+ + iC_4^+X^- \xrightarrow{k_{13}} iC_5^+ + C_6^+X^-$</td>
<td>2-1.9</td>
</tr>
<tr>
<td>$iC_5^+ + HX \xrightarrow{k_{14}} iC_5^+X^-$</td>
<td>2-1.10</td>
</tr>
<tr>
<td>$iC_5^+X^- + iC_4 \xrightarrow{k_3} iC_5^+ + iC_4^+X^-$</td>
<td>2-1.11</td>
</tr>
<tr>
<td>$C_6^+X^- + iC_4 \xrightarrow{k_{4}} C_6^+ + iC_4^+X^-$</td>
<td>2-1.12</td>
</tr>
<tr>
<td>$iC_7^+X^- + C_3^= \xrightarrow{k_{15}} C_{10}^+X^-$</td>
<td>2-1.13</td>
</tr>
<tr>
<td>$C_{10}^+X^- + iC_4 \xrightarrow{k_{8}} C_{10}^+ + iC_4^+X^-$</td>
<td>2-1.14</td>
</tr>
<tr>
<td>$iC_5^+ + iC_4^+X^- \xrightarrow{k_{16}} C_9^+X^-$</td>
<td>2-1.15</td>
</tr>
<tr>
<td>$C_6^+X^- + C_3^= \xrightarrow{k_{17}} C_9^+X^-$</td>
<td>2-1.16</td>
</tr>
<tr>
<td>$C_9^+X^- + iC_4 \xrightarrow{k_{7}} C_9^+ + iC_4^+X^-$</td>
<td>2-1.17</td>
</tr>
<tr>
<td>$C_{10}^+X^- \xrightarrow{k_{18}} iC_5^+ + iC_5^+X^-$</td>
<td>2-1.18</td>
</tr>
</tbody>
</table>
In Table 2-1.3 the self-alkylation reactions are given which form the C₈ isoparaffins. As stated above, these reactions are uniquely coupled to the initiation reactions.

The remainder of the reactions to be considered are the "destructive alkylation reactions" given in Table 2-1.4.

II. Modifications of Schmerling Theory for the Mechanistic Model

The specific modifications to the Schmerling theory for the mechanistic model are presented in the following paragraphs. These modifications involve the C₆, C₈, C₉, C₁₀ and C₁₁ species.

Octane Formation

It is evident that all octanes are not formed by the basic self-alkylation step as presented by Schmerling (29). This only accounts for the trimethylpentanes; whereas dimethylhexanes are probably formed through the mechanism as outlined by Hofmann and Schriesheim (11). This work points toward formation of dimethylhexanes via allylic ions. These ions are derived from the same reactant which forms trimethylpentanes - that is, isobutane. The trimethylpentanes are formed by the combination of the tertiary-butyl carbonium ion with the isobutylene formed via this cation as shown by reaction 2-1.6. The dimethylhexanes are formed from a combination of this in situ formed isobutylene and its ionic counterpart, the allylic ion. For the alkylation of isobutane with propylene, this is just an extension of the self-alkylation of isobutane (see...
Chapter I - "Mechanism"). As the dimethylhexanes make up only 25 to 30% of the total octanes (Table 4-4), the added complications of considering the allylic ion formation and subsequent reactions are not justified for this range of concentrations of the dimethylhexanes.

Another possible route for dimethylhexane formation was given by Kennedy (16) who has shown that dimethylhexanes may be formed through combination of two heptyl ions and subsequent disproportionation to octanes and hexanes. This was demonstrated in the isomerization of dimethylpentanes promoted by isopropyl fluoride-boron trifluoride. However, Hofmann and Schriesheim (11) used results from actual sulfuric acid catalyzed alkylation reactions to support their conclusions on the mechanism of dimethylhexane formation via the allylic ion. For this reason it is felt that the theory of Hofmann and Schriesheim is a more probable mechanism of dimethylhexane formation. Consequently, the assumption that the self-alkylation of isobutane should adequately account for the formation of both the dimethylhexanes and the trimethylpentanes.

**Nonane Formation**

It is apparent from data presented by Cupit, Gwyn, and Jernigan (7) that the nonanes - primarily trimethylhexanes - are formed by the reaction of isopentenes with isobutane (reaction 2-1.15).

There should be formation of nonanes from the combination of
tertiary hexyl ions with propylene also as shown by reaction 2-1.16. However, the extent of each reaction cannot be exactly ascertained by direct measurement. There is more than one route of formation of isopentyl species, equations 2-1.9 and 2-1.18; and, therefore, comparing the yields of isopentane (equation 2-1.18) and hexanes (equation 2-1.12) will not determine the exact contribution of each species to nonane formation due to the reactions 2-1.11 and 2-1.12. Thus, it was necessary to assume that a fraction, X, of the nonanes was formed by the following reaction

\[ \text{iC}_5^+ + \text{iC}_4^+ \text{X}^- \rightarrow \text{C}_9^+ \text{X}^- \]  

(2-1.15)

with the remainder being formed by:

\[ \text{C}_6^+ \text{X}^- + \text{C}_3^+ \rightarrow \text{C}_9^+ \text{X}^- \]  

(2-1.16)

The best value of X may be selected by determining the best fit for the mathematical model on an Arrhenius plot as various values of X are assumed. It will be shown by the following discussion that X must have a value which is greater than 0.5 and less than or equal to 1.0.

As will be seen in the results in Table 4-4, the molar yield of isopentane increased from a concentration that was approximately equal to that of the hexanes at 81°F. to a concentration that was 50% greater than hexanes at 135°F. This greater
yield of pentanes at the higher temperatures is caused by the fact that the precursors of isopentane, the isopentyl carbonium ion and isopentene are formed by the reaction

\[
C_{10}^+X^- \rightarrow iC_5^= + iC_5^+X^- \quad 2-1.18)
\]
as well as by the following reaction which also forms all of the hexyl intermediates.

\[
iC_7^= + iC_4^+X^- \rightarrow iC_5^= + C_6^+X^- \quad 2-1.9)
\]

Based on the above reactions, the yield of isopentane should always be higher than that of the hexanes. However, the formation of \(C_9\) competes with the formation of \(C_5\) and \(C_6\) by reactions 2-1.15 and 2-1.16, and this may alter the result expected by considering reactions 2-1.9 and 2-1.18 alone. If \(X\) were equal to 0.5, the \(C_5\) yield would always be the larger of the \(C_5\) and \(C_6\) yield since additional \(iC_5^=\) is formed by reaction 2-1.18. However, the yield of \(C_5\) is essentially equal to the \(C_6\) yield at 81°F., and as a result the formation of \(C_5^=\) by reaction 2-1.18 must be insignificant.

But at 135°F. the \(C_5\) yield was 50% greater than the \(C_6\) yield. For this to be true the \(C_5^=\) formed by reaction 2-1.18 must be significant and consequently give the correspondingly higher \(C_5\) yield.

Additional \(C_5^=\) is also furnished by reaction 2-1.18 for the reaction with \(iC_4^+X^-\) in reaction 2-1.15 to form \(iC_9^+X^-\). Therefore, this
second source of \( iC_5^- \) requires that \( X \) have a value greater than 0.5. Finally, the upper bound on \( X \) is 1.0 which corresponds to all of the nonane formed by reaction 2-1.15.

**Decane Formation**

The formation of the decyl carbonium ion in the propylene-isobutane system is most logically explained by reaction of a heptyl cation with propylene.

\[
iC_7^+X^- + C_3^+ \rightarrow C_{10}^+X^- \quad 2-1.3
\]

This is the most direct route and has the simplest stochiometry -

\[
2C_3^+ + iC_4^+X^- \rightarrow C_{10}^+X^- \quad 2-1
\]

The formation of the hexyl species has been shown to be via the reaction of a heptyl unsaturate (formed from a heptyl carbonium ion) with the tertiary-butyl cation (**i.e.,** reaction 2-1.9). This is also a source of isopentene which may be subsequently saturated to isopentane by reaction 2-1.11. However, as will be shown in the data of this work and that of Shlegeris (31), the heavy ends (such as decanes) decrease in yield with increase in temperature with a corresponding increase in isopentane and hexane yields. The latter cannot be explained through equation 2-1 alone. It is evident that cracking of the decyl ion to isopentene and a pentyl carbonium ion must be occurring to explain at least part of the
additional pentanes formed. This is reaction 2-1.18 in Table 2-1.4

\[ C_{10}^{+}X^{-} \rightarrow iC_{5}^= + iC_{5}^{+}X^{-} \]  

2-1.18

and it has been proposed both by Schmerling (29) and by Kennedy (16). This would also explain the reduction in yield of decanes.

**Undecane Formation**

In this work the chromatogram peaks in the C\textsubscript{11} range were generally so minute that a quantitative analysis was not possible. A weathered sample from a run at one of the lower temperatures (81°F) and low acid concentration (90-91%) was run by the Chromatograph Laboratory of the Esso Research and Engineering Company at Baytown, Texas. The amount of C\textsubscript{11} present was less than 4.0%. This sample on weathering had a 75% decrease in volume, and thus, this figure should be reduced by 1/4 of that obtained by ER&E to represent the reactor concentration. Also, with the exception of the C\textsubscript{12} (which was less than 1.0%), this was the smallest concentration present in the sample. All of this would imply that the C\textsubscript{11} species may be omitted without introducing noticeable error in calculation of rate constants. This allows the two reactions

\[ iC_{7}^= + iC_{4}^{+} \rightarrow C_{11}^{+} \]  \[ C_{11}^{+} \rightarrow C_{6}^{+} + iC_{5}^= \]  

2-2)  

2-3)
to be reduced to a single reaction by the elimination of the undecyl ion, and the equation used in the model is

$$iC_7^- + iC_4^+X^- \rightarrow C_6^+X^- + iC_5^- \quad 2-1.9)$$

Other Reactions

There are two other reactions presented in Chapter I which were not included in the model. The first is the formation of methylpentanes via dimerization of propylene. This would be expected if reaction conditions were such that high propylene concentrations existed at points within the reactor. However, under well-mixed conditions with the catalyst pre-saturated with isobutane these conditions would have little likelihood of occurring. Also, Kennedy (16) has shown that 2, 3-dimethylbutane will isomerize to 2- and 3-methylpentane to yield a hexane fraction very similar to that found in butene alkylates. The 2, 3-dimethylbutane is the expected hexyl species from reaction 2-1.9. Consequently, from the work of Kennedy this would be the source of methylpentanes and not dimerization of propylene.

The other reaction which was not included in the model is

$$C_8^+ \rightarrow iC_5^- + C_3^+ \quad 2-4)$$

The primary reason for this is that a secondary cation is formed and stability arguments (see Chapter I - "Mechanism") would disfavor...
this reaction. Other scission reactions occur which form secondary cations, but these cations may immediately isomerize to the tertiary form while the propyl species cannot.

III. Rate Equations and the Mathematical Model

The overall rates of formation of each species may now be written having the mechanistic model specified. The net rates of the intermediates (both ions and unsaturates) will be taken as zero in a steady state balance. This may be done as none of these species are fed into the reactor nor do they appear in the hydrocarbon product. Also, the rate of degradation of the acid is small enough to consider that the intermediates' buildup in the acid may be neglected. It should be noted, too, that it is standard practice in kinetic analysis to set the net rates of formation of intermediates to zero.

For a continuous, stirred tank reactor, the overall rates are time independent when the reactor is operated at steady state. For this heterogeneous system the reaction rates are in moles per unit volume catalyst per unit time. The concentrations are expressed as moles per unit volume of catalyst. The rate constants are in units that correspond to these. By the usual convention the rate of production of a chemical species is taken as positive.

The rate equations are presented in Tables 2-2.1 through 2-2.5 for the chemical reactions listed in Tables 2-1.1 through 2-1.4. In
Table 2-2.1 the reactant consumption rates are given. These are actually material balances on the reactants and are linear combinations of other rate equations. The rate equations in Table 2-2.2 serve primarily to relate the product formation rates to the rate equations of Tables 2-2.3 through 2-2.5 as will be subsequently discussed.

In Tables 2-2.3 and 2-2.4 the olefinic and ionic rate equations are given. Together with the equations in Table 2-2.5 they comprise the alkylation kinetic model and thus serve as the basis for the derivation of the mathematical model to permit the computation of the reaction rate constants from the experimental data. There are a total of eighteen equations which can be used to solve for the eighteen rate constants. The concentrations of the isoparaffins, olefins and ions have yet to be dealt with, however.

Attempts to eliminate the ionic and olefinic intermediates from the rate equations result in equations in which the following quantities may be evaluated: \( k_1 (k_{11}/k_9) \), \( (k_{12}/k_5) \), \( (k_{15}/k_{12}) \), \( (k_{16}/k_{14}k_9) \), \( (k_{17}/k_4) \), \( (k_{18}/k_8) \). The constants \( k_2 \), \( k_3 \), \( k_6 \), \( k_7 \), \( k_{10} \) and \( k_{13} \) may not be evaluated in such a scheme as discussed in Appendix A. To solve for any of the individual rate constants appearing in the ratios would require an estimate of the concentration of the reaction intermediates.

Since the test of the validity of the model is to determine
**TABLE 2-2.1**

**Material Balance on Reactants**

**and Associated Consumption Rates**

\[-r_{C_4} = \pm_{C_4} = k_2 [C_3^+X^-][iC_4] + k_3 [iC_5^+X^-][iC_4] + k_4 [C_6^+X^-][iC_4] + k_5 [iC_7^+X^-][iC_4] + k_6 [C_8^+X^-][iC_4] + k_7 [C_9^+X^-][iC_4] + k_8 [C_10^+X^-][iC_4] + k_9 [C_4] + k_{10} [C_10^+]\]  

\[-r_{C_3} = -P_{C_3} = k_1 [C_3^{\cdot\cdot\cdot}][HX] + k_{11} [iC_4^+X^-][C_3^{\cdot\cdot\cdot}] + k_{15} [iC_7^+X^-][C_3^{\cdot\cdot\cdot}] + k_{17} [C_6^+X^-][C_3^{\cdot\cdot\cdot}]\]  

2-2.1)

2-2.2)
### Table 2-2.2

**Product Formation Equations**

\[
\begin{align*}
\text{r}_{C_3} &= P_{C_3} = k_2 [C_3^+ X^-][iC_4] \\
\text{r}_{C_5} &= P_{C_5} = k_3 [iC_5^+ X^-][iC_4] \\
\text{r}_{C_6} &= P_{C_6} = k_4 [C_6^+ X^-][iC_4] \\
\text{r}_{C_7} &= P_{C_7} = k_5 [iC_7^+ X^-][iC_4] \\
\text{r}_{C_8} &= P_{C_8} = k_6 [iC_8^+ X^-][iC_4] \\
\text{r}_{C_9} &= P_{C_9} = k_7 [C_9^+ X^-][iC_4] \\
\text{r}_{C_{10}} &= P_{C_{10}} = k_8 [C_{10}^+ X^-][iC_4]
\end{align*}
\]
TABLE 2-2.3

Olefinic Intermediate Rate Equations

\[ r_{iC_4} = 0 = k_9 [iC_4^+X^-] - k_{10} [iC_4^=] [iC_4^+X^-] \]  \hspace{1cm} 2-2.10)

\[ r_{iC_5} = 0 = k_{13} [iC_7^=] [iC_4^+X^-] + k_{18} [C_{10}^+X^-] \\
- k_{14} [iC_5^=] [HX] - k_{16} [iC_5^=] [iC_4^+X^-] \]  \hspace{1cm} 2-2.11)

\[ r_{iC_7} = 0 = k_{12} [iC_7^+X^-] - k_{13} [iC_7^=] [iC_4^+X^-] \]  \hspace{1cm} 2-2.12)
**TABLE 2-2.4**

**Carbonium Ion Rate Equations**

<table>
<thead>
<tr>
<th>Ion Equation</th>
<th>Rate Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{C_3^+} )</td>
<td>( 0 = k_1[C_3^=][HX] - k_2[C_3^+X^-][iC_4] ) 2-2.13</td>
</tr>
<tr>
<td>( r_{iC_4^+} )</td>
<td>( 0 = r_{iC_4} - k_9[iC_4^+X^-] - k_{10}[iC_4^+X^-][iC_4^=] - k_{11}[iC_4^+X^-][C_3^=] - k_{13}[iC_7^=][iC_4^+] - k_{16}[iC_7^=][iC_4^+] ) 2-2.14</td>
</tr>
<tr>
<td>( r_{iC_5^+} )</td>
<td>( 0 = k_{14}[iC_5^=][HX] + k_{18}[C_{10^+X^-}] - k_3[iC_5^+X^-][iC_4] ) 2-2.15</td>
</tr>
<tr>
<td>( r_{C_6^+} )</td>
<td>( 0 = k_{13}[iC_7^=][iC_4^+] - k_{17}[C_6^+X^-][C_3^=] - k_4[C_6^+X^-][iC_4] ) 2-2.16</td>
</tr>
<tr>
<td>( r_{C_7^+} )</td>
<td>( 0 = k_{11}[iC_4^+X^-][C_3^=] - k_5[iC_7^+X^-][iC_4] - k_{15}[iC_7^+X^-][C_3^=] ) 2-2.17</td>
</tr>
<tr>
<td>( r_{iC_8^+} )</td>
<td>( 0 = k_{10}[iC_4^+X^-][iC_4^=] - k_6[iC_8^+X^-][iC_4] ) 2-2.18</td>
</tr>
<tr>
<td>( r_{C_9^+} )</td>
<td>( 0 = k_{16}[iC_5^=][iC_4^+X^-] + k_{17}[C_6^+X^-][C_3^=] - k_7[C_9^+X^-][iC_4] ) 2-2.19</td>
</tr>
<tr>
<td>( r_{C_{10}^+} )</td>
<td>( 0 = k_{15}[iC_7^+X^-][C_3^=} - k_{18}[C_{10^+X^-}] - k_5[C_{10^+X^-}][iC_4] ) 2-2.20</td>
</tr>
</tbody>
</table>
**Table 2-2.5**

**Special Rate Equations**

\[ \begin{align*}
\text{rr}_C^9 &= k_{16}\left[iC_5^+\right]\left[iC_4^+X^-\right] \quad 2-2.21) \\
(1 - x)r_C^9 &= k_{17}\left[C_6^+X^+\right]\left[C_3^-\right] \quad 2-2.22) \\
\text{ri}_C^5 - r_C^6 + (2x - 1)r_C^9 &= 2k_{18}\left[C_{10}^+X^-\right] \quad 2-2.23)
\end{align*} \]
whether all the mechanistic rate constants obey the Arrhenius relationship, the individual rate constants are needed. The derivation of the kinetic model has assumed the concentrations of the various species used are measurable. This is not actually the case as these concentrations are those of the hydrocarbons in the acid. It is not possible to measure the hydrocarbon concentration in the catalyst phase and only the hydrocarbon phase concentrations can be measured. Therefore, the concentrations in the acid phase must be estimated or computed. Consequently, the following paragraphs will present the derivation of the model for the rate constants in terms of the concentrations in the acid phase. Then the procedures used to compute the concentrations in the acid phase from a knowledge of the concentrations in the hydrocarbon phase will be presented.

**Derivation of the Mathematical Model**

The rate equations of Tables 2-2.1 through 2-2.5 may be solved for the eighteen reaction rate constants. Simple algebraic manipulation and substitution are the only mathematical tools needed.

The following derivations will be done in the order of the numbering of the rate constants. The steps in the derivations will be shown only when they are not obvious. Otherwise, only rate equations used will be stated.

By substituting for the expression for $[C_3^+X^-]$ from equation 2-2.13, Table 2-2.4, into equation 2-2.3, Table 2-2.2,
k_1 may be solved for.

\[ k_1 = \frac{rC_3}{[C_3^\equiv][HX]} \quad 2-3.1 \]

Rate constants \( k_2 \) through \( k_8 \) may be obtained from equations 2-2.3 through 2-2.9 in Table 2-2.2 using equation 2-2.6 as an example.

\[ k_5 = \frac{r_iC_7}{[iC_7^\equivX^\equiv][iC_4]} \quad 2-3.2 \quad 3.8 \]

If equation 2-2.10, Table 2-2.3, is added to equation 2-2.18, Table 2-2.4, the sum is:

\[ k_9[iC_4^\equivX^-] - k_6[iC_8^\equivX^\equiv][iC_4] = 0 \quad 2-5 \]

Substituting equation 2-2.7, Table 2-2.2, yields \( k_9 \):

\[ k_9 = \frac{rC_8}{[iC_4^\equivX^\equiv]} \quad 2-3.9 \]

\( k_{10} \) may be obtained by substituting equation 2-2.7, Table 2-2.2, into equation 2-2.18, Table 2-2.4:

\[ k_{10} = \frac{rC_8}{[iC_4^\equivX^\equiv][iC_4^\equiv]} \quad 2-3.10 \]

The remaining rate constants, \( k_{11} \) through \( k_{18} \), may not be solved for until further rate equations are derived, since of the
total of twenty equations in Tables 2-2.1 through 2-2.4, only seventeen are independent. This is illustrated as follows.

Equations 2-2.1 and 2-2.2, Table 2-2.1, are material balances on the reactants propylene and isobutane and are not independent. Equation 2-2.1 is the sum of equations 2-2.3 through 2-2.9. Equation 2-2.2 can be obtained as a linear combination of equations 2-2.3, 2-2.4, 2-2.6, 2-2.9, 2-2.11, 2-2.12, 2-2.13, 2-2.15, and 2-2.20. Equation 2-2.14 is equal to the sum of equations 2-2.15 through 2-2.20.

Seventeen equations remain with which to solve for eighteen rate constants. Thus, one more equation is needed to solve for all of the rate constants. This equation must relate the amount of C9 formed by \( C_6^+X^- \) and the amount formed by \( iC_5^= \). This may be done by writing the following two equations:

\[
x(r_{C_9}) = k_{16}[iC_5^=][iC_4^+X^-] \tag{2-2.21}
\]

\[
(1-x)(r_{C_9}) = k_{17}[C_6^+X^-][C_3^=] \tag{2-2.22}
\]

where \( X \) is the fraction of nonanes formed by reaction of \( iC_5^= \) with \( iC_4^+X^- \) as previously defined. \( X \) is not a variable and is to be determined from a best fit of the experimental data. Adding equations 2-2.21 and 2-2.22 results in the total rate of formation of C9. This is

\[
r_{C_9} = k_{16}[iC_5^=][iC_4^+X^-] + k_{17}[C_6^+X^-][C_3^=]
\]
and using equation 2-2.8 gives equation 2-2.19 of Table 2-2.4.

\[ k_7\left[C_9^{+X^-}\right][iC_4] = k_{16}\left[iC_5^{=}\right][iC_4^{+X^-}] + k_{17}\left[C_4^{+X^-}\right][C_3^{=}] \quad (2-2.19) \]

Thus, equation 2-2.19 is now not independent. The result is eighteen equations, equations 2-7.3 through 2-2.13, 2-2.15 through 2-2.18, and 2-2.20 through 2-2.22, and eighteen unknowns.

However, the derivation of an additional rate equation will be of aid in solving for \( k_{11} \) through \( k_{18} \). This new equation will relate the relative amounts of the pentyl species formed by reactions 2-1.9 and 2-1.18. The hexyl cation is assumed to be formed only by reaction 2-1.9 and to be consumed only in reactions 2-1.12 and 2-1.16. Since the reaction 2-1.16 gives the amount of trimethylhexanes formed via the hexyl ion and the amount of isopentene formed via reaction 2-1.9 is equal to the sum of the \( C_6 \) formed and the \( C_9 \) formed by the hexyl ions, the following rate equation may be written:

\[ k_{13}\left[iC_7^{=}\right][iC_4^{+X^-}] = \left(\frac{r_{iC_5^{=}}}{(2-1,9)}\right) = (1-x)r_{C_9} + r_{C_6} \quad (2-6) \]

This also required using reactions 2-1.16, 2-1.7 and 2-1.12. The amount of isopentane formed from isopentene is the total amount of isopentane formed less that formed by the pentyl cations produced in reaction 2-1.18.
These two equations may be substituted into equation 2-2.11 giving

\[ r_{iC_5} = 0 = (1 - x)r_{C_9} + r_{C_4} - r_{iC_5} + k_{18}[C_{10}^+X^-] + k_{18}[C_{10}^+X^-] - k_{16}[iC_5][iC_4^+X^-] \] 2-8)

but from equation 2-2.21

\[ k_{16}[iC_5][iC_4^+X^-] = Xr_{C_9} \]

substituting the above into 2-8 and rearranging, the final result is:

\[ r_{iC_5} - r_{C_6} + (2x - 1)r_{C_9} = 2k_{18}[C_{10}^+X^-] \] 2-2.23)

This important result will permit the computation of \( k_{18} \) and several intermediate rate constants also.

Table 2-2.5 summarizes the additional rate equations derived above. With the aid of these equations \( k_{11} \) through \( k_{18} \) may be readily obtained as follows.

Adding equations 2-2.17 and 2-2.20 of Table 2-2.4 and substituting equations 2-2.6 and 2-2.9, Table 2-2.1 gives

\[ k_{11}[iC_4^+X^-] C_3 = - r_{iC_7} - k_{12}[iC_7^+X^-] - k_{18}[C_{10}^+X^-] - r_{C_{10}} = 0 \] 2-9)
Substituting equation 2-2.23, Table 2-2.5, results in

\[ k_{11}\left[\text{iC}_4^+\text{X}^-\ \text{C}_3=\right] - r_{\text{iC}7} - r_{\text{C}10} - k_{12}\left[\text{iC}_7^+\text{X}^-\right] \]

\[-\left\{r_{\text{iC}5} - r_{\text{C}6} + (2x - 1)r_{\text{C}9}\right\}/2 = 0 \quad 2-10 \]

Now from equation 2-2.12, Table 2-2.3,

\[ k_{12}\left[\text{iC}_7^+\text{X}^-\right] = k_{13}\left[\text{iC}_7^+=\text{iC}_4^+\text{X}^-\right] \quad 2-2.12 \]

Substituting the above and equations 2-2.5, Table 2-2.1 and 2-2.22, Table 2-2.5, into equation 2-2.16, Table 2-2.4, yields

\[ k_{12}\left[\text{iC}_7^+\text{X}^-\right] = (1 - x)r_{\text{C}9} + r_{\text{C}6} \quad 2-11 \]

Substituting 2-11 into 2-10 gives \( k_{11} \):

\[ k_{11} = \frac{r_{\text{C}7} + r_{\text{C}10} + (r_{\text{C}5} + r_{\text{C}6} + r_{\text{C}9})/2}{\left[\text{iC}_4^+\text{X}^-\right] \left[\text{C}_3=\right]} \quad 2-3.11 \]

Also from equation 2-11 the expression for \( k_{12} \) is

\[ k_{12} = \frac{r_{\text{C}6} + (1 - x)r_{\text{C}9}}{\left[\text{iC}_7^+\text{X}^-\right]} \quad 2-3.12 \]
As $k_{13}[iC_7]=iC_4^+X^-$ is equal to $k_{12}[iC_7^+X^-]$ by equation 2-2.12, the expression for $k_{13}$ is

$$k_{13} = \frac{r_{C_6} + (1-x)r_{C_9}}{[iC_7][iC_4^+X^-]} \quad 2-3.13$$

To obtain $k_{14}$, equation 2-2.15, Table 2-2.4, may be used. The terms $k_3[iC_5^+X^-]$ and $k_{18}[C_{10}^+X^-]$ may be substituted for using equation 2-2.4, Table 2-2.1, and equation 2-2.23, Table 2-2.5, respectively. The result is

$$k_{14} = \frac{r_{iC_5} + r_{C_6} - (2x-1)r_{C_9}}{2[iC_5^=][iC_4^+X^-]} \quad 2-3.14$$

Equation 2-2.20 is the most convenient equation to use for $k_{15}$. Substitutions to use are equations 2-2.9, Table 2-2.1, and 2-2.23, Table 2-2.5. The final expression for $k_{15}$ is

$$k_{15} = \frac{r_{iC_5} - r_{C_6} + (2x-1)r_{C_9} + 2r_{C_{10}}}{2[iC_7^=][C_3^=]} \quad 2-3.15$$

Expressions for $k_{16}$ and $k_{17}$ may be obtained rearranging equations 2-2.21 and 2-2.22, Table 2-2.5, respectively:

$$k_{16} = \frac{r_{C_9}}{[iC_5^=][iC_4^+X^-]} \quad 2-3.16$$

$$k_{17} = \frac{(1-x)r_{C_9}}{[C_6^+X^-][C_3^=]} \quad 2-3.17$$
Similarly, equation 2-2.23, Table 2-2.5, yields $k_{18}$:

$$k_{18} = \frac{r_1c_5 - r_6 + (2x - 1)r_9}{2[C_{10}^+X^-]} \quad 2-3.18$$

Equations 2-3.1 through 2-3.18 are summarized in Table 2-3.1. The reaction rate constants may be obtained from these equations assuming they (the rate constants) are the only unknowns. These will be the values for any one temperature. However, as the reaction rate (and, therefore, the reaction rate constant) increases with increasing temperature, it is necessary to incorporate the magnitude of this increase into any kinetic model.

**Temperature Dependence of the Reaction Rate Constants**

In a homogeneous system, the increase in reaction rate with temperature may be attributed to an increase in the magnitude of the reaction rate constant. This is generally expressed as (18)

$$k_i = k_{0i}T^we^{-E/RT}$$

where

- $k_i$ = the overall reaction velocity constant at any temperature
- $k_{0i}$ = the "frequency factor"
- $E$ = the activation energy for the reaction under consideration
- $R$ = gas constant
\[ T = \text{absolute temperature at which the reaction occurs} \]

\[ w = \text{a constant} \]

The most common way of representing the temperature dependence of the reaction rate constants is by a plot of \( \ln k_i \) vs. \( 1/T \). If \( w \) were not zero

\[
\ln k_i = \ln k_{0i} + w \ln \frac{T-E}{RT} \tag{2-12}
\]

The variation of \( \log k \) with \( T \) would be

\[
\frac{d(\ln k)}{dT} = \frac{w}{T} + \frac{E}{RT^2}
\]

\[
= \frac{wRT + E}{RT^2} \tag{2-13}
\]

Generally, the term \( wRT \) is very small compared to \( E \). Thus, the plot of \( \log k_i \) vs. \( 1/T \) would be linear with a slope of \( (-E/R) \) and an intercept equal to \( \ln k_{0i} \) at \( 1/T \) equal to zero. Thus, the additional complication of considering a value of \( w \) different from zero is not justified within the accuracy of the experimental results.

Then the equation above becomes the well-known Arrhenius relationship (18):

\[
k_i = k_{0i}e^{-E/RT} \tag{2-14}
\]
### Table 2-3.1

**Rate Constant Expressions**

<table>
<thead>
<tr>
<th>Expression</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$k_1 = \frac{r_{C_3}}{[C_3^\ominus][H^\ominus]}$ (2-3.1)</td>
</tr>
<tr>
<td>$k_5$</td>
<td>$k_5 = \frac{r_{iC_7}}{[iC_7^+X^-][iC_4^\ominus]}$ (2-3.2)</td>
</tr>
<tr>
<td>$k_9$</td>
<td>$k_9 = \frac{r_{iC_8}}{[iC_4^+X^-][iC_4^\ominus]}$ (2-3.9)</td>
</tr>
<tr>
<td>$k_{10}$</td>
<td>$k_{10} = \frac{r_{C_8}}{[iC_4^+X^-][iC_4^\ominus]}$ (2-3.10)</td>
</tr>
<tr>
<td>$k_{11}$</td>
<td>$k_{11} = \frac{r_{iC_7} + r_{C_{10}} + (r_{iC_5} + r_{C_6} + r_{C_9})/2}{[iC_4^+X^-][C_3^\ominus]}$ (2-3.11)</td>
</tr>
<tr>
<td>$k_{12}$</td>
<td>$k_{12} = \frac{r_{C_6} + (1-x)r_{C_9}}{[iC_7^+X^-]}$ (2-3.12)</td>
</tr>
<tr>
<td>$k_{13}$</td>
<td>$k_{13} = \frac{r_{C_6} + (1-x)r_{C_9}}{[iC_7^\ominus][iC_4^+X^-]}$ (2-3.13)</td>
</tr>
<tr>
<td>$k_{14}$</td>
<td>$k_{14} = \frac{r_{iC_5} + r_{C_6} - (2x - 1)r_{C_9}}{2[iC_5^\ominus][H^\ominus]}$ (2-3.14)</td>
</tr>
<tr>
<td>$k_{15}$</td>
<td>$k_{15} = \frac{r_{iC_5} - r_{C_6} + (2x - 1)r_{C_9} + 2r_{C_{10}}}{2[iC_7^+X^-][C_3^\ominus]}$ (2-3.15)</td>
</tr>
</tbody>
</table>

(continued)
### TABLE 2-3.1 (continued)

\[
k_{16} = \frac{x r_{C_9}}{[iC_5^=][iC_4^+X^-]} \quad 2-3.16) \\

k_{17} = \frac{(1 - x)r_{C_9}}{[C_6^+X^-][C_3^=]} \quad 2-3.17) \\

k_{18} = \frac{r_{iC_5} - r_{C_6} + (2x - 1)r_{C_9}}{2[C_{10}^+X^-]} \quad 2-3.18)
\]
IV. Estimation of the Concentrations of the Various Species in the Catalyst Phase

Isobutane Concentration in the Catalyst Phase

Estimation of concentrations of the hydrocarbons in the acid phase may be accomplished by use of a suitable equation to describe the rate of mass transfer. This requires a knowledge of the equilibrium solubilities of the various hydrocarbons in the acid phase. The solubilities of the various paraffins could be measured individually, but this is a separate research effort in its own as the solubilities are so very small (7). To date only data on one of the paraffins involved exists. The paraffin is isobutane and the solubility as a function of percent by weight of aqueous sulfuric acid at one temperature is known (7). The maximum solubility is given as 0.001 lb. isobutane/lb. acid for an acid strength of 99.5% at 56°F. However, this would presumably be higher with organic diluents in the acid; Albright (1) has suggested it may be as high as 0.004 lb./lb. in such an acid. The approach taken in this work is consider that the catalyst is saturated with isobutane over the range of isobutane concentrations used in this work. The reasons for this are explained in the following discussion.

The work by Jernigan, Gwyn and Claridge (7) showed that mass transfer area reaches a maximum when all of the hydrocarbon was emulsified. This implies that mass transfer is at a maximum, all other factors being equal - particularly the acid to hydrocarbon
ratio. In a work in which the acid to hydrocarbon ratio is held constant the mole fraction of isobutane in the hydrocarbon is large, and the mass transfer area is at a maximum for this ratio. The concentration of the isobutane at the acid-hydrocarbon interface should be at a constant saturated value, and the mass transfer should be essentially constant. Thus, the concentration of isobutane in the acid phase should be independent of that in the hydrocarbon phase. This can even be more assured if the acid is contacted initially with pure isobutane to bring the isobutane concentration up to a maximum. The conditions described above to insure constant concentration of isobutane are those under which the present research has been carried.

**Propylene Concentration in the Acid Phase**

Propylene, which is very soluble in the acid, would be expected to exhibit concentrations in the acid proportional to the concentration in the feed. Thus, the following model for propylene concentration in the acid was assumed:

\[ [C_3^=]_{\text{acid}} = \text{Constant} \times [C_3^=]_{\text{HC Feed}} \quad 2-15 \]

No temperature dependence was assumed, since none was known.

**Other Paraffin Concentrations in the Acid Phase**

Generally, since the saturates migrate into the acid phase through mass transfer, the values for the concentrations in the acid
phase may be calculated from the following mass transfer equation (19)

\[ N_i = K_{m1}aV \left( \left( \frac{C_{Ci}}{acid} \right) K_{Di} - \left( \frac{C_{Ci}}{HC} \right) \right) \] 2-16)

where

- \( N_i \) = Pounds/hour of species i transferred
- \( K_{m1}a \) = Mass transfer coefficient - lb./hr.-ft.\(^3\)
- \( V \) = Volume of bed - ft.\(^3\)
- \( \left( \frac{C_{Ci}}{acid} \right) \) = Concentration of i lb./lb. acid
- \( \left( \frac{C_{Ci}}{HC} \right) \) = Concentration of i lb./lb. HC
- \( K_{Di} \) = Phase distribution coefficient

\[
K_{Di} = \left( \frac{\left( \frac{C_{Ci}}{HC} \right)}{\left( \frac{C_{Ci}}{acid} \right)} \right) \text{ (at equilibrium)}
\]

\( \left( \frac{C_{Ci}}{acid} \right) \) may be found by rearranging equation 2c.

\[
\left( \frac{C_{Ci}}{acid} \right) = \frac{N_i}{K_{Di}K_{m1}aV} + \left( \frac{C_{Ci}}{HC} \right) \] 2-17)

\( K_D \) for isobutane can be considered as the inverse of the equilibrium solubility of isobutane in sulfuric acid, as \( \left( \frac{C_{Ci}}{HC} \right) \) at equilibrium for any hydrocarbon is equal to unity.

Since no data on solubilities for the other paraffins exist, a relationship must be assumed between the solubility of any paraffin and that of isobutane. As a general rule, heavier hydrocarbons
are less soluble in water than are light ones (9). This should hold for sulfuric acid, since it also is an aqueous medium, but not necessarily in the same proportions as for water. Therefore, it will be assumed that the solubility of a species is a function only of molecular weight. Specifically for this work:

\[
(C_{i\text{acid}}) = f(M_i)
\]

\[
= \frac{(C_{iC_4\text{acid}})(M_i)_{iC_4}}{(M_i)}
\]

As stated in Chapter I, the most accurate way to estimate a mass transfer coefficient for a system such as alkylation is to use data from a non-reacting system with similar physical properties. Such data exists (see Chapter I)(19). The geometry of the reactor used was different in that system from that of the reactor used in this study; however, this should not affect the product of mass transfer coefficient and the interfacial area, \(K_{ma}\), unless the area, \(a\), is significantly different. The only characterization of the emulsion reported was that it was fine and no bubbles could be seen. Assuming this implies that the authors considered they had a near maximum in the term \(a(ft.^2/ft.^3)\), the only difficulty in applying their work directly would be the differences in viscosity. It will be remembered that the corn syrup solution used was to approximate the physical properties of an aluminum halide catalyst. As such,
the viscosity was ten times that of water, but the mass transfer coefficient obtained with the syrup solution was only 47% of that obtained with water. This implies that the mass transfer coefficient was not a strong function of viscosity. Thus, sulfuric acid with a viscosity of about 30 times greater than water would be expected to have an emulsion mass transfer coefficient only slightly lower than that obtained by Malloy and Taylor for a corn syrup solution and heavy alkylate. Since the difference between the coefficient obtained above and the one which exists in the reaction medium of this study is probably small, and since the above coefficient is the only one available for a similar medium, it will be used unchanged in this study. Also, as only one value is known, it must be assumed the same for all the species in this problem. As all the species in the product are saturated isoparaffins except propane, this assumption is probable valid.

**Estimation of Ionic Intermediate Concentrations**

With the concentrations of the reactants and products estimated, there is still the problem of the concentrations of the carbonium ions and intermediate unsaturates.

The carbonium ions will be considered first. Since small cations of this type are relatively unstable as compared to, say, the triphenylmethyl cation, then it is likely that their concentrations are quite low compared to their parent molecules, even in a sulfuric acid
environment. Bethell and Gold (3) indicate that the size of the ion, as well as the location of the "carbonium ion center", influence the stability. However, it is doubtful that the range of sizes of tertiary ions involved (butyl through decyl) is large enough to warrant consideration of differences in stabilities on this basis. Also, temperature should effect carbonium ion stability and, therefore, their concentrations. In what manner, however, is not known, and thus, it cannot be considered here. The main effect on stability is according to whether an ion will be secondary or tertiary. As a generality, secondary ions are an order of magnitude or more less stable than tertiary ions. Also, lacking any other information to the contrary as to stabilities, the molar concentrations of the carbonium ions will be considered a function of the molar concentrations of their parent atoms in the acid phase.

\[
[C_i^+X^-] = f([C_i]) \quad 2-19)
\]

As nothing is known of the function \(f([C_i])\) in sulfuric acid, the simplest form will be selected and this is a simple proportional relationship. Then, the above equation becomes

\[
[C_i^+X^-] = Z[C_i] \quad 2-20)
\]

where \(Z\) is a constant of proportionality. The magnitude of \(Z\), of course, will affect the rate constants' magnitudes in one-to-one
correspondence. For a value of Z of $10^{-7}$ the rate constant for reactions involving carbonium ions in this work vary from $10^5$ to $10^{17}$. Those for the first order rate constants for ion decompositions lie in the range of $10^4$ to $10^6$. Naworski's first order rate constants (25) were in the range of $10^4$ to $10^5$ for butene polymerization. However, the value he assumed for butene solubility in sulfuric acid was probably low as he assumed it to be the same as isobutane. This would cause his rate constants to be high since they are inversely proportional to the butene solubility squared in his model. Thus, a value of Z equal to $10^{-7}$ seems quite reasonable.

This equation (2-26) is sufficient to describe the concentration of all tertiary ions except the tertiary-buty1 carbonium ion which is formed via the initiation reaction. As the only other time this reaction occurs is in conjunction with the formation of octanes, it should be considered as part of the overall sequence:

\begin{align*}
C_3^+ + HX & \xrightarrow{k_1} C_3^+X^- & 2-1.1) \\
C_3^+X^- + iC_4 & \xrightarrow{k_2} iC_4^+X^- + C_3 & 2-1.2) \\
iC_4^+X^- & \xrightarrow{k_9} iC_4^+ + HX & 2-1.5) \\
iC_4^+X^- + iC_4 &= \xrightarrow{k_{10}} iC_8^+X^- & 2-1.6) \\
iC_8^+X^- + iC_4 & \xrightarrow{k_6} iC_8 + iC_4^+X^- & 2-1.7)
\end{align*}
Reactions 2-1.1 and 2-1.2 are the initiation reactions. Until steady state is reached in a continuous reactor, these reactions 2-1.1 and 2-1.2 are responsible for the buildup of tertiary-butyl cations. Reactions such as 2-1.6 and 2-1.7 do not effect the tertiary-butyl ion concentration as the ions are regenerated on a one-to-one correspondence as they are used. Reaction 2-1.5 represents the consumption of butyl cations. If the rates of production and consumption of the carbonium ions are equated,

\[ k_2 [C_3^+X^-][iC_4] = k_9 [C_4^+X^-] \]  

but the net rate of formation of \( C_3^+X^- \) is also zero;

\[ r_{C_3^+X^-} = 0 = k_1 [C_3]=- [HX] - k_2 [C_3^+X^-][iC_4] \]  

2-2.13

thus,

\[ k_9 [iC_4^+X^-] = k_1 [C_3]=- [HX] \]  

b)  

or

\[ [iC_4^+X^-] = \frac{k_1}{k_9} [C_3]=- [HX] \]  

c)

Therefore, the concentration of the tertiary-butyl ions may be considered proportional to the concentration of propylene in the acid phase, due to their buildup via the initiation reaction. This
buildup will occur until steady state is reached where the regeneration of these ions is equal to the consumption.

Knowing the above relation, (c), to determine the value of \([iC_4^+X^-]\) for a value of \([C_3^=]\), the following equations were derived.

Using equation 2-15 to substitute for \([C_3^=]\), (c) becomes:

\[
[iC_4^+X^-]_1 = \frac{k_1}{k_9} \left( C_{C_3^=} \right)_{HC_1} [HX] \times \text{constant} \tag{d}
\]

At the same acid concentration for another value of \(\left( C_{C_3^=} \right)_{HC}[iC_4^+X^-]\) is:

\[
[iC_4^+X^-]_2 = \frac{k_1}{k_9} \left( C_{C_3^=} \right)_{HC_2} [HX] \times \text{constant} \tag{e}
\]

Dividing (e) by (d) the resulting ratio is

\[
\frac{[iC_4^+X^-]_2}{[iC_4^+X^-]_1} = \frac{\left( C_{C_3^=} \right)_{HC_2}}{\left( C_{C_3^=} \right)_{HC_1}}
\]

or

\[
[iC_4^+X^-]_2 = [iC_4^+X^-]_1 \frac{\left( C_{C_3^=} \right)_{HC_2}}{\left( C_{C_3^=} \right)_{HC_1}} \tag{2-21}
\]

Now, \([iC_4^+X^-]_1\) must be used as a base case. The most convenient base case for this work appears to be that one for which \(\left( C_{C_3^=} \right)_{HC_2}\) is the lowest, and then

\[
[iC_4^+X^-]_1 = [iC_4]_1 Z \tag{2-22}
\]
Thus, with this one assumption of a base case, the values of $[iC_4^+X^-]$ for various values of $[C_3=]_{HC}$ may be calculated.

**Concentrations of the Olefinic Intermediates**

The olefinic intermediate concentrations must be similarly deduced. First of all, it is recognized that they must bear some functional relationship to the intermediates from which they were formed. The products which they form must also be a factor. For example, the reaction involving the formation of isobutylene

$$iC_4^+X^- \longrightarrow iC_4^= + HX$$  \hspace{1cm} 2-1.5)

is an indication that the concentration of isobutylene would be

$$[iC_4^=]_{acid} = \left( [iC_4^+X^-]_{acid} \right)$$  \hspace{1cm} 2-23)

That for the consumption of isobutylene is

$$iC_4^+X^- + iC_4^= \longrightarrow iC_8^+X^-$$  \hspace{1cm} 2-1.6)

but the only other reaction involved for $iC_8^+$ is

$$iC_8^+X^- + iC_4 \longrightarrow iC_8^+ + iC_4^+X^-$$  \hspace{1cm} 2-1.7)

Thus, it would seem that

$$[iC_8] = f\left( [iC_4^=] \right)$$  \hspace{1cm} 2-24)
But the concentration of $iC_8$ has been determined by mass transfer, so reversing 2-24,

$$[iC_4^\equiv] = f([iC_8])$$  \hspace{1cm} 2-25

As the form of the functions in 2-23 and 2-25 are not known, they must be estimated. The simplest functional form is a proportion. This is the form which will be used and the actual expression to be used for isobutylene in this work will be

$$[iC_4^\equiv] = (Y_{iC_8})(iC_4^+X^-)$$  \hspace{1cm} 2-26

where $Y_{iC_8}$ is the mole fraction of octanes in the reaction product (excluding isobutane). Assuming that the proportion is the correct form of functional relationship of olefinic intermediates to the other species, the expressions for $iC_7^\equiv$ and $iC_5^\equiv$ may be derived as follows.

The reactions forming $iC_5^\equiv$ are

$$C_{10}^+X^- \rightarrow iC_5^\equiv + C_5^+X^-$$  \hspace{1cm} 2-1.18)

and

$$iC_7^\equiv + iC_4^+X^- \rightarrow iC_5^\equiv + C_6^+X^-$$  \hspace{1cm} 2-1.9)

Thus,

$$[iC_5^\equiv] \propto \left\{ [C_{10}^+X^-] + [iC_7^\equiv] \right\}$$
The final expression is
\[
\left[ iC_5^{=\text{f}} \right] = \left\{ Y_{iC_5} + xY_{C_9} \right\} \left[ iC_7^{=\text{f}} \right] + \left[ C_{10}^{+X^-} \right] \quad 2-27)
\]

For the value of \( iC_7^{=\text{f}} \), the reaction forming it is:
\[
iC_7^{+X^-} \rightarrow iC_7^{=\text{f}} + \text{HX} \quad 2-1.8)
\]

Thus,
\[
\left[ iC_7^{=\text{f}} \right] \neq \left[ iC_7^{+X^-} \right]
\]

The consumption reaction is
\[
iC_7^{=\text{f}} + iC_4^{+X^-} \rightarrow iC_5^{=\text{f}} + C_6^{+X^-} \quad 2-1.9)
\]

and
\[
\left[ iC_7^{=\text{f}} \right] \neq \left\{ 2 \left[ C_6 \right] + \left[ C_9 \right] \right\}
\]

The final expression is
\[
\left[ iC_7^{=\text{f}} \right] = \left\{ 2Y_{iC_6} + Y_{xC_9} \right\} \left[ iC_7^{+X^-} \right] \quad 2-28)
\]

**Summary**

The preceding development will be used with the mathematical model (equations 2-3.1 through 2-3.18) to determine the rate constants for the reaction of isobutane-propylene alkylation in a continuous flow, stirred tank reactor. The variables to be perturbed are temperature, olefin space velocity, and catalyst concentration. The validity of the model is to be tested by the variation of rate
constants with temperature. If the equation

$$\log k_i = \log k_{0i} - \frac{E}{RT}$$

will correlate the variation of the various rate constants with temperature, then the model will be considered valid.

This model, it is felt, will have several advantages over the type of model presented by Jernigan, Gwyn and Claridge (14). First, it is based on a more exact chemistry - no rate constants are considered the same for several reactions. Then, too, all the major components are considered and not lumped into "other alkylate." These properties will allow the prediction of the composition of an alkylate product with respect to the amount of $C_3$ through $C_{10}$.

This model will also predict the quantitative effect of temperature on the product distribution. The qualitative effect of catalyst concentration may also be predicted. These are two variables not considered by the previous model.

The model in this work, however, does assume constant emulsion properties and, thus, is not able to correlate the product distribution change with change in emulsion. The model of Jernigan and coworkers doesn't assume this and does predict variations in product quality with changes in emulsion properties.

The accuracy of the model derived in this chapter is dependent, of course, on the estimations of the various concentrations. However,
its use is not limited to the assumptions made in the estimations. When more data on solubilities, mass transfer, and carbonium ion concentrations relative to paraffin concentrations is available, it may easily be incorporated into the model in its present form.

If other limitations exist for the model, they would be the number possible of reactions for the formation of a species (e.g., nonanes and decanes). Unless fractions of rates were ascribed each reaction as was done for the C₉'s, only one overall route for the formation of each species could be handled by the model. Any limitation caused by this was sought to be minimized by choosing the most logical and mechanistically consistent route of formation for each species to use in the model.
CHAPTER III

EXPERIMENTAL AND ANALYTICAL EQUIPMENT AND PROCEDURES

The only valid test of a mathematical model is to determine if it correlates experimental data correctly as to the existing theory. To test the model presented in Chapter II, data was taken using a small pilot alkylation unit, a custom sampling system, and modern, well-known analytical tools. In discussing the experimental equipment and its operation, it will be convenient to use the above three classes of apparatus and thus the three corresponding phases of operation.

I. Alkylation Pilot Unit

An overall diagram of the alkylation unit is shown in Figure 3-1. In Figure 3-2 the reactor settler is shown. In discussing the primary components (which include (1) the product and feed tanks, (2) the diaphragm feed pump, (3) the reactor, (4) the sample valve, (5) the settler, and (6) the caustic wash vessel), it will make their functions more clear to trace the hydrocarbon acid streams through the entire system. The supporting components (including (1) the reactor temperature control loop, (2) mechanical seal lubrication and cooling loop, (3) the tracer injection valve, and (4) the pressure supply system) will be discussed following the primary components.
FIGURE 3-1
PILOT UNIT FLOW DIAGRAM
FIGURE 3-2
PILOT UNIT REACTOR AND SETTLER
The hydrocarbon reactant mixture is fed from one of two feed tanks. The construction and dimensions of these tanks are shown in Figure 3-3. By gravity the hydrocarbon flows into the suction side of a Lapp, LS-20, diaphragm pump from the feed tanks. This pump has a maximum capacity of 1,040 cc/hr.

The diaphragm pump pumps the hydrocarbon through the tracer injection valve to the bottom of the reactor. Here the hydrocarbon is forced under pressure through a hypodermic needle, the tip of which is placed just under the tip of the turbine (Figure 3-4). Because of this the feed enters into the reactor under a high velocity—about 20 ft./sec. This allows the feed to be immediately dispersed into the acid-hydrocarbon emulsion. Thus, under conditions of high agitation, no high local concentrations of propylene would be expected within the emulsion.

The reactor is constructed of #316 stainless steel, five-inch nominal diameter, 40 gage seamless pipe. The construction and dimensions of the reactor are shown in Figure 3-4. Not shown is the lid and mechanical seal assembly for the turbine shaft.

The design is of a standard, vertical-tube, continuous-flow, stirred-tank reactor. The liquid volume in the reactor is 0.0579 ft.\(^3\). This includes the volume occupied by the turbine and turbine shaft. The turbine is the standard six flat-blade type designed and manufactured by Mixing Equipment Company. The diameter and
2" or 5" Schedule 40 weld caps

2" or 5" Schedule 40 std. steel pipe

1/2" pipe to 1/4" tubing connectors top and bottom

Penberthy valves

5/8" O.D.

"350 psi rated "sight glass"

48"
placement of the turbine is within standard design parameters of mixers.

The reactor is jacketed for heating or cooling. The jacket forms an annular flow region about the periphery of the reactor for upward flow of the heat transfer medium.

The emulsion overflow from the reactor enters the settler (Figure 3-5). Here there is no agitation and negligible flow velocities due to the large area. "Settling" of the acid from the emulsion is thus affected. The clear hydrocarbon overflows out and the acid is recycled to the reactor in a closed loop.

The hydrocarbon product overflows from the settler into a caustic wash vessel (Figure 3-6). Here the product flows over caustic pellets to neutralize any residual acid.

Finally, the hydrocarbon product flows by gravity into the product tanks. These tanks are identical in construction and dimensions to the two feed tanks.

The secondary components have the following functions:
(1) to control the reactor temperature, (2) to lubricate the mechanical seal assembly, (3) tracer injection, and (4) to maintain a pressure on the entire pilot unit.

Reactor Temperature Control Loop

Water was circulated through the jacket of the reactor back through a set of coils immersed in a large (about 40 gallons) water
1/2" x 1 1/2" 316 S.S. flatstock for reinforcement

14.5" I. D. Schedule 40 welded #316 S.S. pipe

1/2" 316 S.S. plate

3 1/2"

Emulsion Hydrocarbon

inlet out

2 1/4"

Acid return 2 5/8"

3 7/8"

BOTTOM VIEW

All nipples

1/2" 316 S.S.

FIGURE 3-5

ACID SETTLER
FIGURE 3-6

CAUSTIC WASH VESSEL
bath. This bath was either cooled with crushed ice or blocks of dry ice or heated via a steam coil routed through it. Fine temperature control was accomplished by varying the amount of bypass around the bath.

**Mechanical Seal Lubrication and Cooling Loop**

A light oil made from blending normal heptane with a 30 weight motor oil was circulated through the mechanical seal assembly, acting as both a coolant and lubricant. It circulated through coils immersed in a one-gallon ice bath for cooling. The cooling system was kept under about 100 psig to aid in the sealing action of the mechanical seal.

**Tracer Injection Valve**

Tracer tests using carbon 14 labeled normal heptane were used to determine the residence time distribution of the reactor. The only practical method of using radioactive tracers to study residence time distributions in stirred tank reactors was to inject a pulse of radioactive material into the reactor and record the amount of radioactivity in the reactor effluent with time. The tracer injection valve shown in Figure 3-7 was designed and built by J. A. Camps (6) to accomplish this. The tracer was drawn into the tracer cavity by a vacuum, the cavity was moved into the path of the feed stream by the action of an air-operated piston, and the feed swept the tracer into the reactor. As the total volume of the
FIGURE 3-7

TRACER INJECTION VALVE
tracer so injected was only about 0.056 in.\(^3\) compared to a reactor volume of 0.0579 ft.\(^3\), this may be considered to be a "pulse" injection.

**The Pressure System**

As will be discussed, the presence of volatile materials in the product required a pressure applied in excess of the vapor pressure of the feed to keep all hydrocarbons in the liquid phase. Even more pressure was required to suppress cavitation from the action of the turbine at high RPM's. To maintain a suitable pressure of 140 to 150 psig, a nitrogen blanket was used. One nitrogen supply system was connected to the feed tanks, reactor, settler, and product tanks by 1/4 inch copper tubing. In this manner all the primary components of the pilot unit were kept at the same pressure. The other nitrogen system was connected to a backpressure regulator on the discharge of the diaphragm pump. This was done to insure that the pump would always pump against a large, constant positive head - a necessity for its proper operation.

**II. Sampling System**

Because a large portion of the alkylate product was composed of hydrocarbons which boil below the operating temperatures, the pilot unit was operated under pressures sufficient to keep these compounds in the liquid phase at the operating temperatures. If a sample is desired which has a composition representative of the
reactor effluent, and thus, of the reactor contents at steady state, it must be taken and stored under a pressure greater than the reactor operating pressure. The sampling system used in this work was custom designed and built for this purpose by Precision Sampling Corporation of Baton Rouge.

The sampling system included (1) the emulsion sample valve assembly - Figure 3-8, (2) the high-pressure sample vials - Figure 3-9, and (3) the Probe Sampler - Figure 3-10. All three of the above devices seal against high pressure by the same mechanism. This involves a hollow shaft through which the liquid flows and Teflon seal fitted snugly around it - see below.

In the "open" position liquid (or gas) may flow in the direction shown or in the opposite direction, depending on the pressure gradient. In the "sealed" position the port is entombed within the Teflon seal so that no flow occurs and the pressure is held.

The emulsion sample valve assembly was located between the reactor and settler as shown in Figure 3-1. It is from this valve that the reactor effluent sample was taken. The assembly consisted of a Precision Sampling Corporation "micro bomb valve"
FIGURE 3-8

EMULSION SAMPLE VALVE ASSEMBLY
FIGURE 3-9

HIGH-PRESSURE SAMPLE VIAL
fitted into a thickwalled sleeve. The valve had an adapter on it which allowed any of the high-pressure vials to be connected to it in a pressure tight manner (see Figure 3-15). The assembly had negligible holdup; thus, no stagnant pools of catalyst were associated with it to contaminate a sample.

The high-pressure sample vials shown in Figure 3-9 were used to collect and store the samples for analysis. They consisted essentially of a high-pressure glass syringe body encased in Teflon. The sealing device previously described was fitted into one end of the syringe body and the other end was permanently sealed. The volume was slightly over five cc. The Teflon incasing had a window with which to observe the sample. The glass was marked in 0.1 cc. divisions and this was used to determine the amounts of hydrocarbon and acid in the sample once the phases had separated.

The "Probe Sampler", shown in Figure 3-10, was used to obtain a sample of the volatile liquid hydrocarbon from the sample vial and inject it into the chromatograph for analysis. The probe has an adapter which allowed it to be connected in a pressure tight manner to a high-pressure sample vial. The needle could be lowered into the hollow shaft of the vial. The shaft would then be lowered until the port was in the hydrocarbon layer of the sample; the needle plunger was then used to withdraw a hydrocarbon sample. Both the needle and the vial would then be sealed again. The Probe
Sampler had a maximum capacity of five microliters. As one microliter was the standard injection for liquids into a gas chromatograph, a spacer was used for this purpose.

III. Analytical Tools

The analytical methods used in this work were gas chromatography and acid-base titration. Chromatography was used for the quantitative and qualitative analyses of the hydrocarbon samples. Titration was the tool used to determine the weight percent $\text{H}_2\text{SO}_4$ in the catalyst.

Gas Chromatography Equipment and Techniques

A Varian Model 1844 gas chromatograph equipped with flame ionization detectors, linear temperature programmer, and a 200 ft. by 0.01 in. open tubular squalane coated column was used to analyze the hydrocarbon samples. This is shown in Figure 3-11. Calibration of this instrument involved injecting samples of known qualitative and quantitative composition, and using the resulting chromatograms as standards. The chromatograms were made on a Honeywell Electronik 16 recorder.

The standard samples included one from the Esso Research Laboratories, Baton Rouge, and one from the Baytown Research Division of Esso Research and Engineering Company, Baytown, Texas. Other standard samples included mixtures of propane, propylene, isobutane, isopentane, 2,2-dimethylbutane, 2, 3-
FIGURE 3-11
GAS CHROMATOGRAPH AND RECORDER
dimethylbutane, 2 and 3 methylpentane, and 2,2,4-trimethylpentane of varying compositions prepared in the Reacting Fluids Laboratory at Louisiana State University.

Each standard was run under the same conditions: initial oven temperature - 2°C. held for 3 1/2 minutes, then programmed at 4°C./min. to 100°C. and held until the entire sample was eluted. Identification was based on relative retention times of the peaks obtained by running the standards supplied the two laboratories of Esso Research and Engineering Company and comparing the chromatograms to those supplied with the samples.

Since all of the components of the alkylate sample were saturated paraffins, no "weight factor" was necessary for calibration with the flame ionization detector of the gas chromatograph. The weight percent, \( W_{p_i} \), was calculated for a sample containing \( N \) components as:

\[
W_{p_i} = \frac{A_i}{\sum_{i=1}^{N} A_i} \times 100\%
\]

where \( W_{p_i} = \) weight percent component \( i \)

\( A_i = \) area of peak corresponding to component \( i \)

The area of the peak was approximated by calculating the area of the triangle formed by drawing the tangent (through the
inflection point) of each side (see Figure 3-12). The use of this method approximated quite well the actual weight percent of each peak in a sample supplied by the Esso Research Laboratories. There were thirty-two components in this sample ranging from $C_5$ to $C_{10}$. The average deviation from using the above method averaged about 3%.

Another method for calculation of peak areas is to multiply the peak height times the width at half the peak height. This was rather difficult to do with the narrow peaks (even at high chart speeds) obtained with a capillary column, and so the above method was used. On some of the broader peaks the latter method was tried to see if any difference (within experimental accuracy) would be obtained in relative peak areas. None was apparent.

The components in the alkylate samples were identified as to both their carbon number and isomeric configuration wherever possible. No unsaturates were found in the samples. It was found that several factors affected the repeatability of the calculated concentrations of the different components. These were the magnitude of the peak area, the shape of the peak, and the number of peaks within a series (for example, the $C_5$ series consisted of one peak; whereas the $C_6$ series consisted of three peaks). For this reason the statistical analyses of the calculated concentrations have been broken down to a basis of carbon number. The results of these
A = 1/2 bh
Wt. % ∝ A

FIGURE 3-12
CALCULATION OF PEAK AREA
analyses are given in Table 3-1.

The 95% confidence limit values in Table 3-1 may be interpreted that 95% of the concentrations will have a percentage variance of less than this value.

**Titration Procedures**

The concentration of the sulfuric acid catalyst was measured before and after each experiment. A five milliliter sample was titrated with a standard and normal NaOH solution. To insure repeatability the pipette was rinsed with distilled water into the beaker containing the acid to be titrated. This was necessary because of the viscous nature of the acid. The indicator used was bromcresol purple with an end point from acid to basic occurring at a pH of 6.8.

The burette used was a standard 50 ml. delivery glass burette. The scale was in 0.1 ml. and could be read to within ±0.05 ml. Normal delivery was about 40 ml. and, therefore, the accuracy of reading was within 0.25%. Successive titrations of the same sample were repeatable to within the same limits.

**Radioactivity Measuring Techniques**

The residence time distribution was measured by injecting a pulse of carbon 14 labeled heptane into the reactor and measuring the radioactivity level of samples of the reactor effluent taken over a period of several mean residence times. The radioactive samples.
### TABLE 3-1

Accuracy of the Gas Chromatographic Analytical Technique

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical Value of the Composition (Wt. Percent)</th>
<th>95% Confidence Limits*(22) (Fraction of Wt. Percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>2.87</td>
<td>.0670</td>
</tr>
<tr>
<td>Isobutane</td>
<td>68.51</td>
<td>.1290</td>
</tr>
<tr>
<td>Isopentane</td>
<td>2.20</td>
<td>.1527</td>
</tr>
<tr>
<td>Hexanes</td>
<td>2.02</td>
<td>.2128</td>
</tr>
<tr>
<td>Heptanes</td>
<td>16.95</td>
<td>.1834</td>
</tr>
<tr>
<td>Octanes</td>
<td>5.45</td>
<td>.1256</td>
</tr>
<tr>
<td>Nonanes</td>
<td>.53</td>
<td>.1844</td>
</tr>
<tr>
<td>Decanes</td>
<td>1.50</td>
<td>.2774</td>
</tr>
</tbody>
</table>

* The 95% confidence limits presented in the results included in this table are from all nine experiments. The first four, however, have more scatter than the last five. The last five had far better repeatability. For example, the average percent deviation for the analysis of isobutane for the first four experiments was 4.16%, while that for the last five was 1.29%. The average percent deviation for the C\textsubscript{10} analysis experiments 1 through 4 was 16.09%; that for 5 through 9 was 5.55%.

The reason for this large difference in deviations appeared to be due to the probe sampler. The sampler was a prototype as originally used, and did not always appear to seal properly. Later, however, it was reworked by the manufacturer and repeatability improved.
were taken over shorter intervals immediately following the tracer injection than later in the experiment. The purpose of this was to characterize the initial portion of the radioactive decay curve (presented in the next section). The residence time distribution function was to be obtained from this curve.

The samples of hydrocarbon containing the tracer were carefully measured as the radioactive count was to be reduced to a counts per unit volume basis. They were then placed in a scintillator solution. This solution consisted of 125 grams of 2, 5-diphenyloxazole (PPO) and 2.5 grams of 1, 4-bio-2-(4-methyl-5-phenyloxazolyl)-benzene dissolved in toluene to make one liter of solution. For details of the sample preparation procedure refer to the work by Camps (6).

These prepared samples were then placed in a Packard Model 2000 Liquid Scintillation Spectrometer for counting. The samples were counted for the minimum time required for an average of $2 \times 10^4$ counts for all the samples corresponding to a 68% confidence limit of ±0.7% of the total count. Results from the residence time distribution measurements are discussed in the next section.

IV. Operating Procedures

In the course of obtaining the experimental data, the following operations were carried out: preparation of the feed blend, preparation of the catalyst, priming the reactor and settler, startup, and
FIGURE 3-13

PACKARD LIQUID SCINTILLATION SPECTROMETER
sampling. The procedures and special equipment involved will be discussed in chronological order with respect to the experimental procedures.

**Preparation of Feed Blend**

The feed blends used were mixtures of propylene and isobutane. These chemicals were supplied by the Matheson Company and each had a minimum purity of 99.0%. The materials came in the form of liquids under their own vapor pressure. Therefore, to remove the isobutane or propylene as a liquid it was necessary to invert and pressurize the cylinder so that (1) the liquid could flow downward and (2) no vaporization of the liquid would occur as the cylinder was emptied. Thus, the isobutane and propylene could be transferred as liquids to the feed blend cylinder.

The feed blend cylinder is shown in Figure 3-14. It was necessary that this cylinder be quite mobile, as the liquid feed had to be agitated very vigorously in this cylinder to insure complete blending of the isobutane and propylene. For this reason, it would have been quite inconvenient to invert this tank valve-down each time it was necessary to fill the feed tanks. Thus, the double valve-standpipe arrangement shown was adapted to the feed blend cylinder. Once the feed was mixed, a nitrogen supply could be connected to the side valve forcing the liquid into the standpipe and out the top valve, which was connected to the feed tanks of the pilot unit.
FIGURE 3-14

FEED BLEND MIX TANK

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
When preparing a feed blend, the mixing cylinder was placed on a set of scales (capacity of 300 pounds) and a predetermined amount of isobutane was weighed in. Then, the more volatile propylene was added. The cylinder was then agitated to mix the components. A sample of this feed blend was subsequently run on the chromatograph for a more precise determination of the proportions of isobutane and propylene.

**Preparation of Catalyst**

Part of this work involved determination of the qualitative effects of the catalyst concentration on the reaction rate constants. To do this the acid had to be diluted with organic materials to simulate a degraded alkylation catalyst. Consequently, a suitable organic diluent had to be selected. Shlegeris (30) noted that an unsaturated C₈ cation may be a source of acid diluents in alkylation. He showed how this ion could undergo isomerization to a trimethylcyclopentenyl cation. In a study entitled "The Fate of the t-Butyl Cation in 96% H₂SO₄" Deno et al. (8) contacted 2,2,4-trimethylpentene (diisobutylene) with 96% sulfuric acid. One-half of the hydrocarbon appeared as saturated products. The other half dissolved into the acid in the form of stable trimethylcyclopentenyl cations. Thus, the acid used in this work was diluted with diisobutylene which forms the trimethylcyclopentenyl ion which Deno claims to be inert to further reaction. All of the sulfuric acid

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
used was contacted first with diisobutylene so that there would
exist no essential differences in catalyst character other than
percent $\text{H}_2\text{SO}_4$. The acid used initially had about 2.3 to 2.5% water.
After diluting the acid, it was titrated to obtain the percent $\text{H}_2\text{SO}_4$.
The dilution and titration was performed until the acid was of the
desired strength. The typical commercial range of acid concentra-
tions is from 98% down to 88%. To simulate this range two
concentrations of the catalyst were selected as 95% and 90%
(weight).

After adding the acid the unit was pressurized to 70 psig,
and the reactor and settler were filled with liquid isobutane up to
the overflow lines. This corresponded to about 8 pounds total of
isobutane. This served two purposes: (1) to act as an initial fill
in the reactor and settler so that physical steady state would be
quickly reached, and (2) so that the acid would be contacted (once
the turbine power was turned on) with pure isobutane and become
saturated with it.

**Start-up**

After the reactor and settler were charged with acid and
isobutane, the stirring motor was turned on and both the seal
coolant pump and the temperature control pump were started.
The reactor temperature was guided to the desired level by either
applying steam or ice to the large water bath. This temperature
was read using either a Leeds and Northrup or Honeywell strip recorder with a Copper-Constantan thermocouple. In either case the temperature measurement was within ±2°F. with calibration.

Once the temperature stabilized at the desired value, the feed was started. (Stabilizing the temperature generally took at least ten minutes, thus allowing the isobutane to begin to saturate the acid.) The approximate volumetric feed rate was determined immediately after the feed was turned on. A feed rate of 12.5 cc./minute was set on the feed pump, but this varied ±0.3 cc./minute for any run and therefore had to be determined by change in feed tank level with time. The exact feed rate was determined by timing level decrease in the small feed tank of about 40 inches. The accuracy with which the level could be measured was about ±0.05 inches at the initial level, and the same for the final level. Thus, the accuracy in determination of the feed rate was within 0.5%. The product rate was measured in the same manner except that the larger product tank was used. Only about 6" difference was measured on this tank making the accuracy of measuring the product rate correct to within about 3%.

**Sampling Procedure**

Sampling was deferred until "steady state" conditions were attained. Reaching this level required three hours from
start-up.* At this time the first sample was taken and the time and reactor temperature recorded. Three other samples then were taken in a like manner in equally spaced intervals within a 20 to 30 minute period, except in the case when a radioactive tracer test was carried out when the sampling period was extended to over two hours. The sampling procedure is illustrated in a series of photographs in Figures 3-15 through 3-18.

V. Summary of Experimental Conditions

The applicability of the mathematical model was tested under a variety of experimental conditions. The variables perturbed were temperature, acid concentration and olefin space velocity. A total of nine experiments were made in which meaningful analyses were obtained. The conditions for these experiments are summarized in Table 3-2.

Several prior experiments were made. However, for various reasons, no meaningful results were obtained. At first 98% sulfuric acid (made using 96% H₂SO₄, "fuming" H₂SO₄ and diisobutylene) was used to catalyze an alkylation reaction using 15% by weight propylene at 50°F. The product from this reaction was

---

* For a hydrocarbon feed rate of 12.5 cc./min. and a hydrocarbon volume in the reactor of 655 cc., this corresponds to about 3 1/2 mean residence times or about 97% of the theoretical steady state level.
FIGURE 3-15

STEP ONE: SAMPLING FROM EMULSION
SAMPLE VALVE ASSEMBLY
FIGURE 3-16

STEP TWO: POST-PRESSURIZING THE SAMPLE VIAL
FIGURE 3-17

STEP THREE: OBTAINING HYDROCARBON SAMPLE
FROM VIAL WITH THE PROBE SAMPLER
FIGURE 3-18

STEP FOUR: INJECTION OF HYDROCARBON SAMPLE INTO GAS CHROMATOGRAPH
## TABLE 3-2

**Summary of Experimental Conditions**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature °F</th>
<th>Olefin Space Velocity</th>
<th>% H₂SO₄ Start</th>
<th>% H₂SO₄ End</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>65</td>
<td>0.104</td>
<td>96.3</td>
<td>95.0</td>
</tr>
<tr>
<td>9</td>
<td>65</td>
<td>0.118</td>
<td>96.4</td>
<td>94.9</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>0.101</td>
<td>90.6</td>
<td>89.3</td>
</tr>
<tr>
<td>6</td>
<td>81</td>
<td>0.185</td>
<td>97.2</td>
<td>92.3</td>
</tr>
<tr>
<td>1</td>
<td>81</td>
<td>0.104</td>
<td>90.7</td>
<td>89.6</td>
</tr>
<tr>
<td>7</td>
<td>105</td>
<td>0.118</td>
<td>96.3</td>
<td>95.2</td>
</tr>
<tr>
<td>4</td>
<td>105</td>
<td>0.105</td>
<td>90.8</td>
<td>89.5</td>
</tr>
<tr>
<td>8</td>
<td>120</td>
<td>0.131</td>
<td>96.4</td>
<td>94.9</td>
</tr>
<tr>
<td>3</td>
<td>135</td>
<td>0.104</td>
<td>96.5</td>
<td>94.2</td>
</tr>
</tbody>
</table>
characterized by the presence of large amounts of heavy compounds in the C₉ plus range which were more than half the total weight of the C₃ plus sample. Three more experiments were also run using the same acid at temperatures ranging from 50 to 70°F. and similar results were obtained. The total run time was about twenty hours and acid samples were collected at the end of each run, but analysis was deferred. At the end of the last run the acid was taken out of the reactor, and its volume appeared to have doubled. Titration of this acid gave a figure of 48% by weight H₂SO₄. Apparently low (in the range of 50°F.) operating temperatures caused this large decrease in catalyst strength by the formation of stable esters within the acid. Birch et al. (4) noticed similar results in their work in attempting to alkylate isobutane with propylene at 20°C. using 97% sulfuric acid as a catalyst. Since this temperature problem was noted and confirmed by the work above the experiments which followed were run with fresh catalyst and at higher temperatures.

Four subsequent experiments were performed, but no meaningful chromatograph analyses were obtained. In the C₉ and C₁₀ range on the chromatograms large "odd-shaped" peaks appeared. These were subsequently identified as acid soluble hydrocarbon compounds which collected in the stems of the sample vials. These impurities were eliminated in subsequent work by withdrawing several samples with the Probe Sampler before one was injected into the chromatograph.
The percent acid in emulsion was maintained at a constant value of 60% by volume. This was controlled by the amount of acid charged into the reactor and was confirmed at 65°F. and 81°F. runs by the relative amounts of acid and hydrocarbon in the sample vials. At higher temperatures the emulsion began breaking at the reactor outlet and thus the relative amounts of acid and hydrocarbon were not a representative of those within the reactor.

Residence Time Distribution Test

The results from the tracer test gave the residence time distribution. This test was carried out with the feed rate and impeller speed the same as the other alkylation experiments. The feed rate was maintained at 12.5 ± 0.3 cc./min. and the impeller speed was 1,700 RPM.

A plot of tracer concentration in counts per minute versus time in hours is shown in Figure 3-19. The line drawn is a least squares fit of the data points.

A general model for mixing in a stirred tank is described as a backmix reactor with bypass, dead space, and plug flow. The equation which describes the decay of a pulse of tracer for this model is

\[ \frac{C}{C_0} = ne^{n(p-0)/m} \]
FIGURE 3-19
RESIDENCE TIME DISTRIBUTION PLOT
FOR ALKYATION REACTOR

$C = 19,480e^{-1.127t}$
where \( C \) = concentration of tracer at any time, \( t \)

\( C_0 \) = initial concentration of tracer

\( \theta \) = dimensionless time, equal to the ratio of the time, \( t \), to the mean residence time, \( t \)

\( n \) = the fraction of the feed which enters the reactor

\( 1-n \) = the amount of bypass

\( p \) = the fraction of the reactor contents which is considered to be in a plug-flow region

\( m \) = the fraction of the reactor contents which is considered to be perfectly mixed

For the above model

\[ m + p + d = 1 \]

where \( d \) is the fraction of the reactor which is dead space. The parameter, \( p \), is the dimensionless time delay until a response from an injection was noticed.

To determine \( p \) the shape of the curve from time zero is needed.

The first data point on the plot in Figure 3-19 was taken at seven minutes. Technical difficulties prevented earlier successful sampling. Thus, only an upper bound on \( p \) can be obtained from this data, i.e.,

\[ p = 7 \text{ mm./}50.4 \text{ min.} = 0.14 \]

However, in the work of Camps (6) using a system that simulated this reactor-settler system the value of \( p \) was found to be zero in a heptane-sulfuric acid emulsion with agitator speeds lower than that used in this test. Therefore, if this conclusion may be applied to this work and the general model reduces to
\[ C = C_0 e^{-n\theta/m} \]

To determine the values of \( n \) and \( m \), the mean residence time, \( \bar{t} \), and the initial tracer concentration is needed. These are given by (18)

\[ \bar{t} = \frac{\int_0^\infty C(t)dt}{\int_0^\infty C(t)dt} \]

\[ C_0 = \frac{\int_0^\infty C(t)dt}{\bar{t}} \]

The value of \( \bar{t} \) may be obtained for this work by graphical integration of Figure 3-1. The result is \( \bar{t} = 50.4 \) minutes.

The value of \( C_0 \) using graphical integration of Figure 3-20 is 20,200 cpm.

A least squares regression analysis on the data points on Figure 3-20 gives

\[ C = 19,480 e^{-1.127t} \]

Combining this equation with the results for \( C_0 \) gives the value of \( n \).

\[ nC_0 = 19,480 \text{ cpm} \]

\[ n = 0.964 \]
Also, since \( t/f = 0 \) the value of \( m \) can be computed in the following manner:

\[
-1.127t = -n\theta E/m = -nt/m
\]

or

\[
1.127 = n/m
\]

and

\[
m = 1.02
\]

These values are accurate to within 10% to 95% confidence limits. Thus, it may be stated that within experimental error the decay equation is

\[
\frac{C}{C_0} = e^{-\theta}
\]

or that the reactor is perfectly mixed.
CHAPTER IV

RESULTS AND CONCLUSIONS

I. Summary of Results

Isobutane was alkylated with propylene with a sulfuric acid catalyst in the small pilot unit described in Chapter III. A series of experiments were performed in which the variables perturbed were temperature, olefin feed concentration, and catalyst strength. The temperature was varied from 65°F. to 135°F., the olefin feed concentration from 12.5 to 22.4% by weight, and the catalyst strengths used were 95 and 90% \( \text{H}_2\text{SO}_4 \) by weight. A more detailed presentation of experimental conditions was shown in Chapter III.

Using the hydrocarbon feed and product distributions (weight percent), the hydrocarbon feed rate (cc./min.), and the sulfuric acid concentration (% \( \text{H}_2\text{SO}_4 \) by weight) the rate constants presented in Chapter II were evaluated for each experiment. The following values of parameters were used: concentration of isobutane in the acid phase \(-7.0 \times 10^{-4}\) lb./lb. \( \text{H}_2\text{SO}_4 \); concentration of propylene for the base case of 12.5% by weight propylene in the feed \(-1.0 \times 10^{-9}\) lb. mole/ft.\(^3\)\( \text{H}_2\text{SO}_4 \); \( A \), the constant relating the proportion of ion concentration per parent species concentration \(-10^{-7}\). As pointed out in Chapter II these values were not completely arbitrary, but rather selected so that the first order reactions in this
work would approximate the order of magnitude observed by Naworski (25). The resulting first order rate constants ranged from $2 \times 10^4$ to $1 \times 10^6$ sec.$^{-1}$. Naworski's rate constant, it will be remembered, was in the order of $10^4$ sec.$^{-1}$. However, the reaction he was studying was the polymerization of butene in sulfuric acid; the analogous reaction in this work was

$$C_3^+ + HX \xrightarrow{k_1} C_3^+X^-$$

2-1.1)

The value of $k_1$ was found to vary between $2.12 \times 10^5$ and $3.09 \times 10^5$ cc./gm. mole-sec. in this work.

The second order rate constants in this work varied from $2 \times 10^5$ to $1 \times 10^{18}$ (cc./gm. mole-sec.). The wide range of values of the second order rate constants was due to the fact that the sulfuric acid was considered a reactant in calculating the values of the rate constants. As its concentration was on the order of $10^4$ to $10^{12}$ times greater than the other reactants, the rate constants for the reactions in which it appeared were very small as compared to the other second order constants.

II. Validity of the Mathematical Model

The model was to be tested by the results obtained at a catalyst strength of 95%. If the rate constants were consistent with the Arrhenius equation, the model was to be considered valid. The
### TABLE 4-1
Results of the Least Squares Fits of the Rate Constants Over the Range of 81 to 135°F. and with a 95% H$_2$SO$_4$ Catalyst

<table>
<thead>
<tr>
<th>Reaction Group</th>
<th>Rate Law</th>
<th>Frequency Factor</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initiation</strong></td>
<td></td>
<td>(cc. (gm. mole-sec.; sec.$^{-1}$))</td>
<td>(Kcal./gm. mole)</td>
</tr>
<tr>
<td>C$_3^+$ + HX $\rightarrow$ k$_1$ C$_3$$^+$X$^-$</td>
<td>k$_{AB}$</td>
<td>1.01 x 10$^7$</td>
<td>2.35</td>
</tr>
<tr>
<td>C$_3$$^+$X$^-$ + iC$_4$ $\rightarrow$ k$_2$ C$_3$ + iC$_4$$^+$X$^-$</td>
<td>k$_{AB}$</td>
<td>2.07 x 10$^{11}$</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Primary</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iC$_4$$^+$X$^-$ + C$<em>3^+$ $\rightarrow$ k$</em>{11}$ iC$_7$$^+$X$^-$</td>
<td>k$_{AB}$</td>
<td>1.99 x 10$^{17}$</td>
<td>2.36</td>
</tr>
<tr>
<td>iC$_7$$^+$X$^-$ + iC$_4$ $\rightarrow$ k$_5$ iC$_7$ + iC$_4$$^+$X$^-$</td>
<td>k$_{AB}$</td>
<td>4.20 x 10$^{10}$</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Self-Alkylation</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iC$_4$$^+$X$^-$ $\rightarrow$ k$_9$ iC$_4^+$ + HX</td>
<td>k$_A$</td>
<td>3.92 x 10$^4$</td>
<td>0.40</td>
</tr>
<tr>
<td>iC$_4$$^+$X$^-$ + iC$<em>4^+$ $\rightarrow$ k$</em>{10}$ iC$_8$$^+$X$^-$</td>
<td>k$_{AB}$</td>
<td>5.63 x 10$^{19}$</td>
<td>4.10</td>
</tr>
<tr>
<td>iC$_8$$^+$X$^-$ + iC$_4$ $\rightarrow$ k$_6$ iC$_8$ + iC$_4$$^+$X$^-$</td>
<td>k$_{AB}$</td>
<td>5.35 x 10$^{10}$</td>
<td>0.0</td>
</tr>
</tbody>
</table>

(contd.)
<table>
<thead>
<tr>
<th>Reaction Group</th>
<th>Rate Law</th>
<th>Frequency Factor</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{cc.} )</td>
<td>(Kcal./gm. mole)</td>
</tr>
</tbody>
</table>

### Destructive Alkylation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Law</th>
<th>Frequency Factor</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>( iC_7^+X^- \rightarrow k_{12} \rightarrow iC_7^= + HX )</td>
<td>( kA )</td>
<td>( 7.49 \times 10^5 )</td>
<td>1.08</td>
</tr>
<tr>
<td>( iC_7^= + iC_4^+X^- \rightarrow k_{13} \rightarrow iC_5^= + C_6^+X^- )</td>
<td>( kAB )</td>
<td>( 3.64 \times 10^{21} )</td>
<td>5.73</td>
</tr>
<tr>
<td>( iC_5^= + HX \rightarrow k_{14} \rightarrow iC_5^+X^- )</td>
<td>( kAB )</td>
<td>( 1.62 \times 10^{11} )</td>
<td>3.69</td>
</tr>
<tr>
<td>( iC_5^+X^- + iC_4 \rightarrow k_3 \rightarrow iC_5 + iC_4^+X^- )</td>
<td>( kAB )</td>
<td>( 3.29 \times 10^{10} )</td>
<td>0.0</td>
</tr>
<tr>
<td>( C_6^+X^- + iC_4 \rightarrow k_4 \rightarrow iC_6 + iC_4^+X^- )</td>
<td>( kAB )</td>
<td>( 4.04 \times 10^{10} )</td>
<td>0.0</td>
</tr>
<tr>
<td>( iC_7^+X^- + C_3 \rightarrow k_{15} \rightarrow C_10^+X^- )</td>
<td>( kAB )</td>
<td>( 3.72 \times 10^{17} )</td>
<td>2.59</td>
</tr>
<tr>
<td>( C_10^+X^- + iC_4 \rightarrow k_8 \rightarrow C_10 + iC_4^+X^- )</td>
<td>( kAB )</td>
<td>( 6.68 \times 10^{10} )</td>
<td>0.0</td>
</tr>
<tr>
<td>( iC_5^= + iC_4^+X^- \rightarrow k_{16} \rightarrow C_9^+X^- )</td>
<td>( kAB )</td>
<td>( 4.26 \times 10^{19} )</td>
<td>2.65</td>
</tr>
<tr>
<td>( C_6^+ + C_3 \rightarrow k_{17} \rightarrow C_9^+X^- )</td>
<td>( kAB )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>( C_9^+X^- + iC_4 \rightarrow k_7 \rightarrow C_9 + iC_4^+X^- )</td>
<td>( kAB )</td>
<td>( 6.02 \times 10^{10} )</td>
<td>0.0</td>
</tr>
<tr>
<td>( C_{10}^+X^- \rightarrow k_{18} \rightarrow iC_5^= + iC_5^+X^- )</td>
<td>( kA )</td>
<td>( 4.45 \times 10^{11} )</td>
<td>8.40</td>
</tr>
</tbody>
</table>
apparent activation energies involved are given. It should be noted that in every case except for $k_2$ through $k_8$ the activation energy was positive, indicating that the reaction rate constants increase with temperature in keeping with reaction rate theory. The activation energies obtained for $k_2$ through $k_8$ were equal to zero within the limits of experimental error. This was to be expected due to the assumptions of constant mass transfer coefficient and isobutane concentration. The values of $k_2$ through $k_8$ were calculated from the following type of equation, e.g., $k_3$.

\[
k_3 = \frac{r_{iC_5}}{[iC_5]^2[iC_4]}^{2-3.3}
\]

The rate $r_{iC_5}$ is the concentration of $iC_5$ in the hydrocarbon phase times the product flow rate. Also, the concentration of $iC_5$ in the acid phase is calculated by the mass transfer equation below.

\[
(C_{iC_5})_{acid} = \frac{N_{iC_5}}{K_{D_{iC_5}}K_m} + \frac{(C_{iC_5})_{HC}}{K_{D_{iC_5}}} \quad 2-17
\]

where $N_{iC_5}/V$ is equal $r_{iC_5}M_{iC_5}$. $M_{iC_5}$ is the molecular weight of $iC_5$.

Now the value of $r_{iC_5}$ in terms of $(C_{iC_5})_{HC}$ is

\[
r_{iC_5} = \frac{N_{iC_5}}{V(M_{iC_5})} = \frac{(C_{iC_5})_{HC}W}{V(M_{iC_5})} \quad 4-1
\]
where $W$ is the mass flow rate of the product stream. Substituting this into equation 2-17, the result is

$$\left( C_1C_5 \right)_{\text{acid}} = \frac{N_iC_5}{V} \left( K_{D_iC_5} K_{m^a} + \frac{V}{WK_{D_iC_5}} \right) \quad 4-2$$

or dividing by $M_iC_5$ and multiplying by $\rho_{\text{acid}}$ the density of the acid, the expression above becomes

$$\left[ C_1C_5 \right] = \frac{N_iC_5 \rho_{\text{acid}}}{V(M_iC_5)} \left( \frac{1}{K_{D_iC_5} K_{m^a}} + \frac{V}{WK_{D_iC_5}} \right)$$

$$= r_iC_5 \left( \frac{1}{K_{D_iC_5} K_{m^a}} + \frac{V}{WK_{D_iC_5}} \right) \rho_{\text{acid}} \quad 4-3$$

Substituting this result into equation 2-3.3, noting that $[iC_5^+X^-]$ is equal to $[iC_5]Z$

$$k_3 = \frac{r_iC_5}{[iC_5]Z[iC_4]}$$

$$= \frac{r_iC_5/Z[iC_4]}{r_iC_5 \left( \frac{1}{K_{D_iC_5} K_{m^a}} + \frac{V}{WK_{D_iC_5}} \right) \rho_{\text{acid}}}$$

or

$$k_3 = \frac{1}{Z[iC_4] \left( \frac{1}{K_{D_iC_5} K_{m^a}} + \frac{V}{WK_{D_iC_5}} \right) \rho_{\text{acid}}} \quad 4-4$$

The mass transfer coefficient was constant as were the concentration of $iC_4$, the values of $Z$, $V$, $W$, $\rho_{\text{acid}}$, and the phase distribution.
Thus, the rate constants \( k_2 \) through \( k_8 \) were not a function of temperature. Although this is an approximation, it does point out that these hydride transfer reactions are not a strong function of temperature.

In Figures 4-1 through 4-10 the Arrhenius plots of the experimentally measured rate constants \( k_1 \) and \( k_9 \) through \( k_{18} \) and the associated linear least squares line are given. The experimental rate constants are given in Table 4-2.

In Figure 4-1 the Arrhenius plot for \( k_1 \) is given. The average of the deviations of the four experimental values from the values predicted by the least squares fit of the data was 8.4%. This rate constant belongs to the reaction which forms propane. In the range of from 81 to 135°F. it varies from a value predicted from the correlation of 1.97 to 2.81 \( \times 10^5 \) cc./gm.mole-sec. This predicts an increase in the yield of propane with temperature, which is consistent with the experimental data.

In Figure 4-2 the Arrhenius plot of \( k_9 \) is shown. The average of absolute deviations of the experimental rate constants from those predicted by the least squares fit was 5.0%. This is the rate constant of the first reaction in the "Self-Alkylation" series. As shown in Table 4-1, this rate constant is characterized by a relatively low frequency factor and activation energy. The low activation energy indicates that the yield of octanes is not as strong a function of
<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Rate Law</th>
<th>81°F</th>
<th>105°F</th>
<th>120°F</th>
<th>135°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁ x 10⁻⁵</td>
<td>kAB</td>
<td>2.12</td>
<td>2.10</td>
<td>2.40</td>
<td>3.09</td>
</tr>
<tr>
<td>k₉ x 10⁻⁴</td>
<td>kA</td>
<td>1.95</td>
<td>2.14</td>
<td>2.26</td>
<td>2.00</td>
</tr>
<tr>
<td>k₁₀ x 10⁻¹⁶</td>
<td>kAB</td>
<td>5.92</td>
<td>7.53</td>
<td>9.46</td>
<td>10.9</td>
</tr>
<tr>
<td>k₁₁ x 10⁻¹⁵</td>
<td>kAB</td>
<td>3.81</td>
<td>4.39</td>
<td>5.42</td>
<td>5.21</td>
</tr>
<tr>
<td>k₁₂ x 10⁻⁵</td>
<td>kA</td>
<td>1.25</td>
<td>1.31</td>
<td>1.41</td>
<td>1.46</td>
</tr>
<tr>
<td>k₁₃ x 10⁻¹⁷</td>
<td>kAB</td>
<td>2.50</td>
<td>3.78</td>
<td>4.39</td>
<td>6.16</td>
</tr>
<tr>
<td>k₁₄ x 10⁻⁸</td>
<td>kAB</td>
<td>3.38</td>
<td>4.49</td>
<td>4.81</td>
<td>6.10</td>
</tr>
<tr>
<td>k₁₅ x 10⁻¹⁵</td>
<td>kAB</td>
<td>5.27</td>
<td>5.36</td>
<td>5.62</td>
<td>8.32</td>
</tr>
<tr>
<td>k₁₆ x 10⁻¹⁷</td>
<td>kAB</td>
<td>5.25</td>
<td>6.21</td>
<td>5.73</td>
<td>8.53</td>
</tr>
<tr>
<td>k₁₈ x 10⁻⁵</td>
<td>kA</td>
<td>3.34</td>
<td>7.14</td>
<td>8.43</td>
<td>12.40</td>
</tr>
</tbody>
</table>
Figure 4-1. Arrhenius plot of the experimentally determined values of the reaction rate constant, \( k_1 \), and the corresponding least squares fit.
Figure 4-2. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_9$, and the corresponding least squares fit.
temperature as are the yields of the other products. The relatively large difference between the activation energies of \( k_1 \) and \( k_9 \) (that for \( k_1 \) being much larger) show that at the higher temperatures of this work the rate of formation of \( C_3 \) is significantly larger than that for \( iC_8 \). This is not the case at lower temperatures (45 - 65°F.) as discussed by Schmerling (29) where the rates of formation are about equal.

In Figure 4-3 the temperature behavior of \( k_{10} \) is shown.

The average absolute deviation of the experimental data from the least squares regression analysis is 1.8%. This reaction rate constant describes the rate of the second reaction in the self-alkylation sequence. The activation energy is much higher for \( k_{10} \), 4.10 Kcal./gm. mole than for \( k_9 \), 0.40 Kcal./gm. mole. Also, the species \( iC_4^= \) formed in the first reaction and consumed in the second reaction does not appear in any other reactions. As a result of this, the constants \( k_9 \) and \( k_{10} \) are not independent as can be seen from equation 2-2.10 below.

\[
\frac{k_9}{k_{10}} = [iC_4^=] \quad 2-2.10
\]

Thus, the self-alkylation sequence resulting in the formation of \( C_8^+X^- \) consists of two interrelated reactions.

The rate constant associated with reaction 2-1.3, the first and most important reaction of the primary alkylation sequence, \( k_{11} \),
Figure 4-3. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_{10}$, and the corresponding least squares fit.
is shown as a function of temperature in Figure 4-4. This reaction is responsible for the formation of not only the dimethylpentanes, but also isopentane, the hexanes, nonanes, and decanes, since all the latter are formed through destructive alkylation reactions. The average absolute deviation of the experimental values of $k_{11}$ from the least squares regression is 4.2%.

The destructive alkylation reactions may be illustrated as a "diverging branch" of side reactions of the heptyl carbonium ion which is shown below in terms of the numbers of the reactions:

\[
\begin{align*}
\text{iC}_4^+X^- + \text{C}_3^- & \xrightarrow{2-1.3} \text{iC}_7^+X^- \\
\text{iC}_7 & \xrightarrow{2-1.8} \text{iC}_5^+X^- \\
\text{C}_6^+X^- + \text{iC}_5^- + \text{iC}_9^+X^- & \xrightarrow{2-1.10} \text{C}_{10}^+X^- \\
\text{C}_6 & \xrightarrow{2-1.12} \text{C}_9^+X^- \\
\text{C}_9 & \xrightarrow{2-1.17} \text{iC}_5^-
\end{align*}
\]

Reaction 2-1.3 was discussed above. Next in importance to reaction 2-1.3 in the branched sequence above are reactions 2-1.8 and 2-1.13.

The reaction rate constant associated with reaction 2-1.8, $k_{12}$, is
Figure 4-4. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_{11}$, and the corresponding least squares fit.
shown as a function of temperature in Figure 4-5. The activation energy associated with \( k_{12} \) approximates that of \( k_9 \) which corresponds to the other reaction of the form

\[
C_i^+X^- \longrightarrow C_i^+ + HX
\]

The average absolute of the \( k_{12} \) experimental values deviation from the correlation predictions is 0.81%.

The reaction rate constant, \( k_{13} \), is shown in Figure 4-6, and the absolute deviation is 3.4%. It may be shown to be related to \( k_{12} \) by rearranging equation 2-2.12.

\[
\frac{k_{13}}{k_{12}} = \frac{[iC_7^=][iC_4^+]}{[iC_7^+]} \quad 4-5)
\]

This is similar to the relation between \( k_9 \) and \( k_{10} \) (equation 2-2.10). Therefore, the formation of \( C_5 \) and \( C_6 \) intermediates are due to two interrelated reactions. These are:

\[
iC_7^+X^- \xrightarrow{k_{12}} iC_7^= + HX \quad 2-1.8)
\]

\[
iC_7^= + iC_4^+X^- \xrightarrow{k_{13}} iC_5^= + C_6^+X^- \quad 2-1.9)
\]

The rate constant, \( k_{14} \), is shown in Figure 4-7. The reaction which forms the isopentyl carbonium ions reflects the formation of isopentane. The isopentyl cations only appear in the reactions shown below.
Figure 4-5. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_{12}$, and the corresponding least squares fit.
Figure 4-6. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_{13}$, and the corresponding least squares fit.
Figure 4-7. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_{14}$, and the corresponding least squares fit.
\begin{align*}
  &iC_5 + HX \xrightarrow{k_{14}} iC_5^+X^- \quad 2-1.10) \\
  &iC_5^+X^- + iC_4 \xrightarrow{k_3} iC_5 + iC_4^+X^- \quad 2-1.11)
\end{align*}

The activation energy associated with \( k_{14} \) is about 30\% higher than that associated with \( k_{16} \) (to be discussed in a later paragraph) which is the other reaction of isopentene. The average absolute deviation of the experimental values from the least squares predictions is 2.9\%.

In Figure 4-8 \( k_{15} \) as a function of temperature is shown. The scatter in the experimental data is comparatively large with an average absolute deviation of 11.6\%. Determination of \( k_{15} \) by equation 2-3.15 is subject to errors which may be compounded due to the complexity of the equation. However, the activation energy and frequency factor are about the same as that for \( k_{11} \), which is the rate constant of an analogous reaction. These similar reactions are

\begin{align*}
  &iC_4^+X^- + C_3 \xrightarrow{k_{11}} iC_7^+X^- \quad 2-1.3) \\
  &iC_7^+X^- + C_3 \xrightarrow{k_{15}} C_{10}^+X^- \quad 2-1.13)
\end{align*}

This reaction (2-1.13) is responsible for the second "branch" (see the discussion of \( k_{12} \)) of destructive alkylation reactions.

Equation 2-1.15 describes \( C_9 \) formation. The reaction rate constant associated with this reaction, \( k_{16} \), is shown in Figure 4-9 as a function of temperature. The activation energy is 2.65 Kcal.
Figure 4-8. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_{15}$, and the corresponding least squares fit.
Figure 4-9. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_{16}$, and the corresponding least squares fit.
The average absolute deviation for $k_{16}$ is 8.5%.

The scission of the decyl ion is described by reaction 2-1.18. It is a first order reaction and, as can be seen from a plot of $k_{18}$ in Figure 4-10, the associated rate constant is a strong function of temperature. This is typical of cracking reactions in general. The activation energy of this rate constant, 8.40 Kcal./gm. mole, was the highest found of all the rate constants in this work. The average absolute deviation for $k_{18}$ was 5.9%.

III. The Effect of Temperature and Olefin Feed Concentration on Distribution Using a 95% $H_2SO_4$ Catalyst

In Figures 4-11 through 4-18 the effect of temperature and olefin feed concentration on conversion and product distribution is shown. These are graphs of predicted values using the least squares analysis values of the rate constants. The method of calculation involved using equations 2-3.1, 2-3.3 through 2-3.9, 2-3.11, 2-3.12, 2-3.14 through 2-3.16, and 2-3.18 to calculate the concentration in the hydrocarbon phase. A derivation of this method is presented in Appendix C. As a general rule the values of concentrations of the products predicted are within about 10% of the experimental values. The reason for these deviations is due to scatter in experimental data. As previously discussed, the maximum of the absolute deviations of the experimentally determined rate constants from the least squares fits was only 11.6% and the lowest 0.8% with the average being 5.0%.
Figure 4-10. Arrhenius plot of the experimentally determined values of the reaction rate constant, $k_{18}$, and the corresponding least squares fit.
Figure 4-11. The predicted pounds of product yield per pound of olefin fed as a function of temperature using 95% H$_2$SO$_4$ and 0.143 lb./lb. feed.
The Effect of Temperature

The effect of temperature on total product yield for the case of 95% sulfuric acid and an olefin feed concentration of 14.3% by weight is shown in Figure 4-11. This concentration of \( \text{C}_3 \) corresponds to a volumetric ratio of isobutane to olefin of 5.55 to 1.0.

The yield is equal to the weight of product per unit weight of olefin fed. This includes propane but not unreacted isobutane. The predicted yield increased considerably over the range of 80 to 135°F - from 1.74 to 2.31. This increase appears to be substantially linear with temperature as shown in Figure 4-11.

Shlegeris (31) noted a similar increase in yield from 25°C (77°F.) to 40°C (104°F.). His yield was defined as "grams of \( \text{C}_5 \) plus per 100 grams of olefin fed." The yield was 169 grams per 100 grams at 25°C and 215 grams per 100 grams at 40°C. He alkylated isobutane with propylene under the following conditions: 2,000 RPM, ratio of isobutane to propylene 5.7:1, concentration of sulfuric acid - 99.3%, 60% acid in the emulsion. A 60 second residence time was used in a 24 ml, reactor-settler combination.

The yield Shlegeris obtained was slightly higher than that of this work even though he employed a much shorter residence time. This may have been due to the rapid reaction to form the secondary products since only about one-third of his product was the product dimethylpentane. However, on the same \( \text{C}_5 \) plus basis the heptanes
in this work made up nearly 60% of the product. The differences may be due to differences in the degree of mixing. The mixing in this work was that of a perfectly mixed stirred reactor. Shlegeris did not state his degree of mixing; however, when he increased his agitation speed to 3,000 RPM, the fraction of heptanes increase to nearly 50%. This implied that the degree of mixing he obtained at 2,000 RPM, the speed used for the above results, was not ideal. Shlegeris stated that "up to perhaps 10% of the propylene was converted to propane; in this work, however, the figure is about 20%. Since including propane serves to reduce the yield of product, subtracting about one pound from the propylene for every pound of propane formed in this work gives yields which are very close but 2-5% lower than those reported by Shlegeris. Another reason for Shlegeris' higher yields may have been the higher acid concentration he used.

It is perhaps unusual to compare the results of works in which there exists such a large difference in contact times. However, the research by Shlegeris represents the only data, to date, which has covered nearly the same range of temperatures and olefin concentrations in the feed while using pure propylene as the feed olefin. Thus, his work represents the only truly valid work with which to compare our results. Also, in a two-phase, liquid-liquid complex reacting mixture, such as alkylation, conversion need not be a strong function
of residence time. Mosby (23) showed that tripling the contact time resulted in only about 15% increased conversion. The additional contact time of experiment as compared to another may serve mainly to allow isomerization reactions time to occur.

In Figure 4-12 the effect of temperature on the yield of heptanes and octanes per pound of product is shown. These products are those which are commercially more desirable due to their high octane members.

The C_7 fraction - the primary product - remained constant at about 0.52 weight fraction. However, in the iC_5 plus product it tapers off slightly from a predicted 0.60 lb./lb. at 80°C to about 0.58 lb./lb. at 90°C and above. It did not show the pronounced decrease as did the yield of heptanes in the work of Shlegeris in the range of 77 to 104°C. This again may have been due to differences in mixing.

In Figure 4-13 the effect of temperature on the yields of light (lighter than heptanes) products is shown. Propane, it may be seen, remains substantially constant. This shows that the yield of propane is not necessarily equimolar to that of octanes as previously indicated. It is actually much higher as the reaction temperature approaches 135°C by Schmerling (29). There may be another reason. The reaction forming C_9

\[ \text{iC}_5^+ + \text{iC}_4^+ \text{X}^- \rightarrow \text{C}_9^+ \text{X}^- \quad (2-1.15) \]
Figure 4-12. The predicted weight fraction of $iC_7$ and $iC_8$ in the product as a function of temperature using 95% $H_2SO_4$ and 0.143 lb./lb. feed.
Figure 4-13. The predicted weight fraction of $C_3$, $iC_5$ and $C_6$ in the product as a function of temperature using 95% $H_2SO_4$ and 0.143 lb./lb. feed.
requires that propane be formed equimolar with \( C_9 \). This was shown on page of Chapter I. However, the molar yields of \( C_9 \) are not large enough to account for all of the extra propane formed. Evidently the initiation sequence is more prominent than just as an initiation step as was originally thought by Schmerling (29).

The yield of \( iC_5 \) is seen to increase almost 80% over the range from \( 80^\circ F. \) to \( 135^\circ F. \). The fact that this increase was much greater than that for the hexanes would substantiate that isopentane precursors are formed by at least one more reaction in addition to

\[
C_7^= + iC_4^+X^- \rightarrow iC_5^= + C_6^+X^- \quad 2-1.9)
\]

namely,

\[
C_{10}^+X^- \rightarrow iC_5^= + iC_5^+X^- \quad 2-1.18)
\]

In Figure 4-14 the predicted values of \( C_9 \) are shown to gradually rise with temperature. In the same figure \( C_{10} \) on the other hand, is seen to rise, peak in the range of 105 to \( 120^\circ F. \), and then begin to decline.

Shlegeris noted a decrease from 34.3 to 32.8% of "heavy ends" when the change of temperature from \( 77^\circ F. \) to \( 104^\circ F. \) occurred. Over about the same range the predicted decrease from this work
Figure 4-14. The predicted weight fraction of
$C_9$ and $C_{10}$ in the product as a
function of temperature using 95%
$H_2SO_4$ and 0.143 lb./lb. feed.
was from 29.5 to 26.8%. However, this was due to the decrease in $C_8$ only as $C_9$ and $C_{10}$ both increased over this range. The results presented by Shlegeris, however, were implied to be due to decrease in olefin polymerization products. This was probably the case in Shlegeris' work due to the lower degree of mixing. No olefin products were found in this work.

**The Effect of Olefin Feed Concentration Variation**

The predicted product yield is shown as a function of the olefin feed concentration in Figure 4-15. It will be seen that an approximate 75% increase in the propylene concentration resulted in about a 45% increase in yield. This increase can be explained with the following discussion. First, recall that the concentration of the tertiary-butyl carbonium ion is proportional to the concentration of propylene in the feed as shown by equation 2-21 with $[C_3^\equiv]$ equal to $(C_{C_3^\equiv})_{HC} \times 8 \times 10^{-9}$.

$$[iC_4^+X^-] = (C_{C_3^\equiv})_{HC} \frac{8 \times 10^{-9} [iC_4^+] Z}{[C_3^\equiv]_{base}}$$ (4-6)

A result of increasing the olefin feed concentration is a corresponding increase in not only the olefin concentration in the acid, but
Figure 4-15. The predicted pounds of product yield per pound of olefin fed as a function of the weight fraction of propylene in the feed at 105% and using 95% H₂SO₄.
an increase in the tertiary-butyl ion concentration, also. Increasing both of these concentrations effects the increase of the rate of formation of all of the product species. Therefore, an increased yield would be obtained as predicted.

The predicted weight fraction of the heptanes and octanes are shown in Figure 4-16 as a function of olefin feed concentration. The yield of heptanes, the primary products, increased about 8% with a 75% increase in propylene feed concentration, whereas the yield of octanes decreased about 35% over the same range. The same reasoning applies for the increase in heptane concentration, due to the increase in tertiary-butyl carbonium ion concentration as a result of the increase in olefin feed concentration. See equation 4-6. On the other hand, the rate of formation of octanes increase but more slowly than the other rates.

\[ r_{iC_8} = k_9[iC_4^+X^-] \]  

Thus, the rate of formation of the octanes is only a function of the tertiary-butyl carbonium ion concentration and not the olefin also. Thus, the octane yield as a fraction of the total product yield would be expected to decrease with increasing propylene concentration. This is shown in Figure 4-16.

In Figure 4-17 the predicted yield of light products, \( C_3 \), \( C_5 \), and \( C_6 \), as a function of propylene feed concentration is shown. The
Figure 4-16. The predicted weight fraction of iC₇ and iC₈ in the product as a function of the weight fraction of propylene in the feed at 105°F, and using 95% H₂SO₄.
Figure 4-17. The predicted weight fraction of $C_3$, iC$_5$ and C$_6$ in the product as a function of the weight fraction of propylene in the feed at 105°F. and using 95% H$_2$SO$_4$. 
propane yield shows the same 35% decrease for a 75% increase in propylene concentration as did the octane yield. The rate of propane formation

\[ r_{C_3} = k_1[C_3][HX] = k_1 \times 8 \times 10^{-9}(C_3)^{2.1}_H C \]  

is a function only of the propylene concentration in the feed. Thus, the propane yield as a fraction of the total product yield would decrease.

As can be seen, the predicted yield of C₆ increases slightly with propylene concentration. The rate of formation of C₆ is given by:

\[ r_{C_6} = k_{12}[iC_7]^+X^- \]  

The formation of products via the species iC₇⁺X⁻ increases with both the increase in propylene concentration and the increase in tertiary-butyl cation concentration. Thus, as was the case for iC₇, the yield of C₆ as a fraction of the product should increase. This is shown in Figure 4-17. The yield increased about 8% with a 75% increase in olefin feed concentration, the same as that of C₇.

The yield of C₅ as a function of propylene concentration was interrelated to those of C₉ and C₁₀. Thus, it should be discussed in that context. The olefin concentration dependent yields of C₉ and C₁₀ are shown in Figure 4-18. The rate of formation of C₁₀ is
Figure 4-18. The predicted weight fraction of $C_9$ and $C_{10}$ in the product as a function of the weight fraction of propylene in the feed at 105°F, and using 95% $H_2SO_4$. 
(subtracting equation 2-3.18 from 2-3.14)

\[ r_{C_{10}} = k_{14}[iC_{7}^+X^-][C_3^-] \]

\[ - k_{18}[C_{10}^+X^-] \quad 4-7 \]

Thus, the rate of formation of \( C_{10} \) is dependent to a higher order of the propylene concentration than \( C_6 \) and \( C_7 \), since the species \( iC_7^+X^- \) reacts with propylene to form the precursor of \( C_{10} \), namely \( C_{10}^+X^- \). This is shown in Figure 4-18 - the yield of \( C_{10} \) increased almost 90% with an increase in propylene feed concentration of 75%.

The rate of formation of \( C_5 \) is (equation 2-3.18 plus equation 2-3.12 minus equation 2-3.16),

\[ r_{C_5} = k_{18}[C_{10}^+X^-] + k_{12}[C_7^+X^-] \]

\[ - k_{16}[iC_5^-][iC_4^+X^-] \quad 4-8 \]

or by substitution of equations 2-2.5 and 2-2.8 into the above

\[ r_{iC_5} = k_{18}[C_{10}^+X^-] + r_{C_6} - r_{C_9} \quad 4-9 \]

The yield of isopentane should increase since it is the sum of terms which increase minus a term, \( r_{C_9} \), which is small compared to the other rates of formation. This is shown in Figure 4-17, where a
75% increase in propylene concentration resulted in a 22% increase in the yield of iC₅.

Since iC₅⁻ is related to the yield of iC₅, the predicted yield as a fraction of the products of C₉ should increase also, as the rate of formation of C₉ is:

\[ r_{C_9} = k_{16}[iC_5^=][iC_4^+X^-] \] 2-3.16

This increase is shown in Figure 4-18.

By way of summarizing the predictions presented in Figures 4-11 through 4-18, it may be stated, based on the data of this work, that while conversion increases with increase in both temperature and propylene concentration in the feed, the product quality suffers. With increase in temperature both isopentane and the hexanes increase; however, the desirable dimethylpentanes remain essentially constant and the high quality octanes (chiefly trimethylpentanes) actually decrease. This is accompanied by a general increase in the C₉'s and C₁₀'s which are generally undesirable from a commercial standpoint of view.

An increase in propylene concentration causes a slight increase in C₅, C₆ and C₇; however, a decrease of octanes similar to that accompanied by an increase in temperature is experienced. Also, the slight increase in the yield of heptanes is negated by the large increases in the yields of the lower quality C₉'s and and C₁₀'s.
The decrease in product quality with increased temperature has previously been ascribed to decrease in octanes (24), increased polymer formation, and high acid degradation (7) (15). While this work confirms the decrease in octanes, there was no indication of polymerization of the olefin to heavy unsaturates in the gas chromatographic analysis. Only slightly higher acid consumption was noted, as seen in Table 3-2 in Chapter III. The reactor used in this work was essentially an ideal, perfectly mixed, stirred tank. As most commercial reactors balance the extent of mixing with the power costs, the resulting degree of mixing can cause polymer formation and acid degradation. Thus, it would seem that proper mixing would become more important at higher temperatures.

High ratios of isobutane to olefin (low olefin feed concentrations) of 5 to 1 by volume or better have been previously felt as a necessity to suppress olefin polymer formation (7) (15). However, again, this is probably due to inadequate mixing. The degree of mixing would certainly become a critical variable at high olefin feed concentrations in order to minimize high local olefin concentrations. In this work successful alkylation was carried out at an isobutane to propylene ratio of about 3 to 1, and no propylene polymers were identified. Thus, the principal reason for lower product quality in this work was higher concentration of \( C_9 \) and \( C_{10} \) in conjunction with lower concentrations of octanes.
IV. Experimental Results at 65°F. Compared to Predicted Values

In Table 4-3 the comparisons of the experimental rate constants with the predicted values at 65°F. are shown using data from Experiment 9. Two experiments were made at this temperature, 2 and 9. However, Experiment 2 was one of the first experiments and difficulties in the sampling technique at that time make the results of Experiment 9 more accurate than 2. The results of Experiment 2 are qualitatively the same as Experiment 9, however.

In order to compare the results shown in Table 4-3, the product distribution obtained at 65°F. should be compared to those at higher temperatures. The product distributions are shown in Table 4-4. Of particular interest to this discussion are the values obtained in Experiment 6, run at 81°F., 95% H₂SO₄, and an olefin feed concentration of 22.4% by weight; in Experiment 8, run at 120°F., 95% H₂SO₄, and an olefin feed concentration of 14.3%; and in Experiment 9, run at 65°F., 95% H₂SO₄ and an olefin feed concentration of 14.3%.

An examination of the yields of the C₉'s and C₁₀'s of these three experiments reveals some surprising facts. The model predicted increases in the rates of formation of both C₉ and C₁₀ with temperature. However, it will be seen in Table 4-4 that at 65°F. the rates of formation of both these species, C₉ and C₁₀, increased instead of decreasing. The increase was almost three
TABLE 4-3
Comparison of Experimental and Predicted Values for the Rate Constants at 65°F. Using a 95% H<sub>2</sub>SO<sub>4</sub> Catalyst

<table>
<thead>
<tr>
<th>Rate Constant</th>
<th>Rate Law</th>
<th>Predicted from Least Squares Fit (cc. gm. mole-sec.; sec. &lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Obtained from Experiment 9 (cc. gm. mole-sec.; sec. &lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k&lt;sub&gt;1&lt;/sub&gt;</td>
<td>kAB</td>
<td>1.75 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1.34 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;2&lt;/sub&gt;</td>
<td>kAB</td>
<td>2.11 x 10&lt;sup&gt;11&lt;/sup&gt;</td>
<td>2.11 x 10&lt;sup&gt;11&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;3&lt;/sub&gt;</td>
<td>kAB</td>
<td>3.47 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
<td>3.45 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;4&lt;/sub&gt;</td>
<td>kAB</td>
<td>4.13 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
<td>4.12 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;5&lt;/sub&gt;</td>
<td>kAB</td>
<td>4.80 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
<td>4.79 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;6&lt;/sub&gt;</td>
<td>kAB</td>
<td>5.47 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
<td>5.46 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;7&lt;/sub&gt;</td>
<td>kAB</td>
<td>6.15 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
<td>6.14 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;8&lt;/sub&gt;</td>
<td>kAB</td>
<td>6.82 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
<td>6.81 x 10&lt;sup&gt;10&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;9&lt;/sub&gt;</td>
<td>kA</td>
<td>1.98 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>1.79 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;10&lt;/sub&gt;</td>
<td>kAB</td>
<td>4.73 x 10&lt;sup&gt;16&lt;/sup&gt;</td>
<td>7.43 x 10&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;11&lt;/sub&gt;</td>
<td>kAB</td>
<td>3.39 x 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>5.56 x 10&lt;sup&gt;15&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;12&lt;/sub&gt;</td>
<td>kA</td>
<td>1.12 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>9.28 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;13&lt;/sub&gt;</td>
<td>kAB</td>
<td>1.84 x 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>3.05 x 10&lt;sup&gt;17&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;14&lt;/sub&gt;</td>
<td>kAB</td>
<td>2.79 x 10&lt;sup&gt;8&lt;/sup&gt;</td>
<td>1.55 x 10&lt;sup&gt;8&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;15&lt;/sub&gt;</td>
<td>kAB</td>
<td>4.25 x 10&lt;sup&gt;15&lt;/sup&gt;</td>
<td>1.28 x 10&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;16&lt;/sub&gt;</td>
<td>kAB</td>
<td>4.42 x 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>1.37 x 10&lt;sup&gt;18&lt;/sup&gt;</td>
</tr>
<tr>
<td>k&lt;sub&gt;17&lt;/sub&gt;</td>
<td>kAB</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>k&lt;sub&gt;18&lt;/sub&gt;</td>
<td>kA</td>
<td>2.27 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>2.35 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
<table>
<thead>
<tr>
<th>Catalyst Concentration (% H₂SO₄)</th>
<th>95</th>
<th>95</th>
<th>90</th>
<th>90</th>
<th>95</th>
<th>95</th>
<th>90</th>
<th>95</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°F)</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>81</td>
<td>81</td>
<td>105</td>
<td>105</td>
<td>120</td>
<td>135</td>
</tr>
<tr>
<td>Olefin Space Velocity (hr⁻¹)</td>
<td>0.104</td>
<td>0.118</td>
<td>0.101</td>
<td>0.104</td>
<td>0.185</td>
<td>0.131</td>
<td>0.105</td>
<td>0.117</td>
<td>0.104</td>
</tr>
<tr>
<td>Run Number</td>
<td>2</td>
<td>9</td>
<td>5</td>
<td>1</td>
<td>6</td>
<td>7</td>
<td>4</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>C₃</td>
<td>1.69</td>
<td>1.59</td>
<td>2.40</td>
<td>1.98</td>
<td>3.88</td>
<td>2.83</td>
<td>2.28</td>
<td>2.87</td>
<td>3.20</td>
</tr>
<tr>
<td>iC₄</td>
<td>67.75</td>
<td>69.83</td>
<td>79.10</td>
<td>74.85</td>
<td>49.85</td>
<td>67.66</td>
<td>72.22</td>
<td>68.51</td>
<td>76.41</td>
</tr>
<tr>
<td>iC₅</td>
<td>0.70</td>
<td>0.97</td>
<td>0.76</td>
<td>0.65</td>
<td>2.66</td>
<td>2.07</td>
<td>1.26</td>
<td>2.20</td>
<td>1.93</td>
</tr>
<tr>
<td>23 DMB</td>
<td>0.72</td>
<td>0.63</td>
<td>0.46</td>
<td>0.48</td>
<td>1.61</td>
<td>1.01</td>
<td>0.75</td>
<td>1.02</td>
<td>0.69</td>
</tr>
<tr>
<td>2 MP</td>
<td>0.52</td>
<td>0.42</td>
<td>0.26</td>
<td>0.20</td>
<td>0.84</td>
<td>0.60</td>
<td>0.38</td>
<td>0.65</td>
<td>0.51</td>
</tr>
<tr>
<td>3 MP</td>
<td>0.16</td>
<td>0.15</td>
<td>0.12</td>
<td>0.09</td>
<td>0.37</td>
<td>0.27</td>
<td>0.16</td>
<td>0.29</td>
<td>0.23</td>
</tr>
<tr>
<td>Total C₆</td>
<td>1.00</td>
<td>1.24</td>
<td>0.84</td>
<td>0.77</td>
<td>2.82</td>
<td>1.88</td>
<td>1.29</td>
<td>1.96</td>
<td>1.43</td>
</tr>
<tr>
<td>24 DMP</td>
<td>5.16</td>
<td>5.24</td>
<td>3.54</td>
<td>4.68</td>
<td>13.95</td>
<td>8.57</td>
<td>7.39</td>
<td>8.20</td>
<td>6.01</td>
</tr>
<tr>
<td>3 MC₆</td>
<td>0.30</td>
<td>0.37</td>
<td>0.22</td>
<td>0.21</td>
<td>0.67</td>
<td>0.64</td>
<td>0.50</td>
<td>0.87</td>
<td>0.90</td>
</tr>
<tr>
<td>Total C₇</td>
<td>17.59</td>
<td>16.29</td>
<td>10.95</td>
<td>14.16</td>
<td>27.84</td>
<td>17.34</td>
<td>16.37</td>
<td>16.95</td>
<td>12.07</td>
</tr>
<tr>
<td>224 TMP</td>
<td>1.47</td>
<td>1.38</td>
<td>0.85</td>
<td>0.87</td>
<td>2.85</td>
<td>2.35</td>
<td>1.58</td>
<td>2.00</td>
<td>1.31</td>
</tr>
<tr>
<td>25 DMH</td>
<td>0.56</td>
<td>0.54</td>
<td>0.34</td>
<td>0.42</td>
<td>0.74</td>
<td>0.59</td>
<td>0.45</td>
<td>0.71</td>
<td>0.59</td>
</tr>
<tr>
<td>223 TMP</td>
<td>0.48</td>
<td>0.54</td>
<td>0.30</td>
<td>0.34</td>
<td>0.78</td>
<td>0.63</td>
<td>0.38</td>
<td>0.74</td>
<td>0.57</td>
</tr>
<tr>
<td>234 TMP</td>
<td>0.61</td>
<td>0.57</td>
<td>0.37</td>
<td>0.43</td>
<td>0.78</td>
<td>0.66</td>
<td>0.66</td>
<td>0.55</td>
<td>0.37</td>
</tr>
<tr>
<td>233 TMP</td>
<td>0.59</td>
<td>0.58</td>
<td>0.34</td>
<td>0.39</td>
<td>1.00</td>
<td>0.89</td>
<td>0.67</td>
<td>0.75</td>
<td>0.52</td>
</tr>
<tr>
<td>23 DMH</td>
<td>0.23</td>
<td>0.24</td>
<td>0.15</td>
<td>0.21</td>
<td>0.39</td>
<td>0.29</td>
<td>0.23</td>
<td>0.31</td>
<td>0.27</td>
</tr>
<tr>
<td>24 DMH</td>
<td>0.18</td>
<td>0.13</td>
<td>0.17</td>
<td>0.08</td>
<td>0.12</td>
<td>0.07</td>
<td>0.04</td>
<td>0.07</td>
<td>0.14</td>
</tr>
<tr>
<td>Other C₈</td>
<td>0.39</td>
<td>0.31</td>
<td>0.16</td>
<td>0.24</td>
<td>0.56</td>
<td>0.31</td>
<td>0.21</td>
<td>0.32</td>
<td>0.41</td>
</tr>
<tr>
<td>Total C₈</td>
<td>4.51</td>
<td>4.28</td>
<td>2.58</td>
<td>2.98</td>
<td>7.22</td>
<td>5.81</td>
<td>4.22</td>
<td>5.45</td>
<td>4.18</td>
</tr>
<tr>
<td>225 TMC₆</td>
<td>0.30</td>
<td>0.46</td>
<td>0.23</td>
<td>0.31</td>
<td>0.64</td>
<td>0.38</td>
<td>0.27</td>
<td>0.33</td>
<td>0.25</td>
</tr>
<tr>
<td>224 TMC₆</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>334 TMC₆</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>235 TMC₆</td>
<td>0.04</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
<td>0.09</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>334 TMC₆</td>
<td>0.03</td>
<td>0.06</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Other C₉</td>
<td>1.10</td>
<td>0.80</td>
<td>0.38</td>
<td>0.53</td>
<td>0.50</td>
<td>0.18</td>
<td>0.17</td>
<td>0.12</td>
<td>0.13</td>
</tr>
<tr>
<td>Total C₉</td>
<td>1.47</td>
<td>1.37</td>
<td>0.67</td>
<td>0.92</td>
<td>1.30</td>
<td>0.64</td>
<td>0.50</td>
<td>0.53</td>
<td>0.44</td>
</tr>
<tr>
<td>2235 TMC₇</td>
<td>0.04</td>
<td>0.13</td>
<td>0.07</td>
<td>0.10</td>
<td>0.13</td>
<td>0.04</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>224 TMC₇</td>
<td>0.47</td>
<td>0.36</td>
<td>0.23</td>
<td>0.39</td>
<td>0.43</td>
<td>0.14</td>
<td>0.20</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>225 TMC₇</td>
<td>0.24</td>
<td>0.19</td>
<td>0.12</td>
<td>0.25</td>
<td>0.23</td>
<td>0.08</td>
<td>0.19</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Other C₁₀</td>
<td>4.54</td>
<td>3.75</td>
<td>2.29</td>
<td>3.10</td>
<td>3.77</td>
<td>1.49</td>
<td>1.42</td>
<td>1.31</td>
<td>1.04</td>
</tr>
<tr>
<td>Total C₁₀</td>
<td>5.29</td>
<td>4.43</td>
<td>2.71</td>
<td>3.84</td>
<td>4.56</td>
<td>1.75</td>
<td>1.86</td>
<td>1.50</td>
<td>1.18</td>
</tr>
</tbody>
</table>
times over that of the values at 120°F. even though the olefin feed concentration was the same in both cases. Further, inspection will show that the values for C₉ and C₁₀ at 65°F. are actually about the same as those for the experiment run at 81°F. even though the olefin feed concentration at 81°F. was almost 60% greater. This is contrary to the results of the math model. It predicts that both C₉ and C₁₀ would be strong functions of olefin feed concentration.

If the results for Experiments 8 and 9 are further compared in light of what should be predicted by the model for Experiment 9, it will be seen that the concentrations of C₃, C₅, and C₆ of Experiment 9 are too low, whereas those of C₉ and C₁₀ should have decreased but increased instead. These results cause the differences between the experimental and predicted values of the rate constants in Table 4-3. There appears to be a change in the reaction mechanism going from 81°F. down to 65°F. The effect on the model of this change in mechanism will now be discussed.

The rate constants k₂ through k₈ show extremely good agreement. However, this is to be expected since these rate constants as calculated are independent of temperature as shown in equation 4-4.

The value for k₁ calculated by

\[ k₁ = \frac{rc₃}{[C₃][HX]} \]  

2-3.1)
is about 30% below the predicted value. The variable which would cause this is $[C_3=]$ since $[HX]$ was the same as in the other experiments. This would say that the actual value of $[C_3=]$ in the experiment was lower than that used for calculating $k_1$. It is possible that this lower temperature could limit the absorption of propylene into the acid phase and the equation

$$[C_3^\equiv] = 8 \times 10^{-9} (C_{C_3^\equiv})_{HC}$$

would not hold for this temperature.

The experimental value for $k_9$ was also slightly lower than the predicted value. However, it is only low by about 10%, and this is within experimental error. Therefore, it is not possible to determine the effect of a possible change in mechanism.

The value for $k_{10}$ was about 65% higher than predicted. This is not entirely due to a change in mechanism, however. The sequence in which $k_{10}$ appears is

$$iC_4^+X^- \xrightarrow{k_9} iC_4^= + HX \quad 2-1.5)$$

$$iC_4^+X^- + iC_4 = \xrightarrow{k_{10}} iC_8^+X^- \quad 2-1.6)$$

$$iC_8^+X^- + iC_4 \xrightarrow{k_{10}} iC_8 + iC_4^+X^- \quad 2-1.7)$$

Now reaction 2-1.6 is very rapid, and $k_{10}$ is in the order of $10^{12}$ to
\(10^{17}\) cc./gm. mole-sec. Therefore, the \(iC_4^-\) reacts almost instantaneously by reaction 2-1.6. Thus, to obtain a true value for \(k_{10}\) the rate of consumption of \(iC_4^-\) needs to be accurately measured. However, this is not readily done. Rather, \(k_{10}\) was measured from the rate of formation of \(C_8\) which in reality is a measure of the rate of reaction 2-1.5. Thus, the values of \(k_{10}\) would not necessarily agree with the predicted values.

The experimental value for \(k_{11}\) is seen in Table 4-3 to be about 65% higher than its predicted value. The reaction with which it is associated is

\[
iC_4^+X^- + C_3 = \frac{k_{11}}{} iC_7^+X^- \quad 2-1.3)
\]

which is the primary reaction. This large value reflects the large rates of formation of \(C_7, C_9, \) and \(C_{10}\), particularly \(C_9\) and \(C_{10}\).

The rate constant is calculated by

\[
k_{11} = \frac{rC_7 + rC_{10} + (rC_5 + rC_6 + rC_9)/2}{[iC_4^+X^-][C_3^-]} \quad 2-3.11)
\]

The actual value of \([C_3^-]\) has been shown to probably be lower than that used; thus, \([iC_4^+X^-]\) must have been larger than predicted to cause the higher rates of formation of \(C_9\) and \(C_{10}\).

The value of \(k_{12}\) associated with

\[
iC_7^+X^- \xrightarrow{k_{12}} C_7^- + HX \quad 2-1.8)
\]
was slightly low as was \( k_9 \), the rate constant of the analogous reaction 2-1.5. The rate constants of the ionic decompositions to olefins and HX such as reaction 2-1.8 appear to be most affected by the mechanism change.

The value of \( k_{13} \) was about 65% higher than prediction. It is involved in a similar sequence as was \( k_{10} \).

\[
k_7^+X^- + k_{12} \rightarrow iC_7^- + HX \quad 2-1.8
\]

\[
iC_7^- + iC_4^+ + k_{13} \rightarrow iC_5^- + C_6^+X^- \quad 2-1.9
\]

Reaction 2-1.9 is also a fast reaction - \( k_{10} \) is in the order of \(10^{17}\) cc./gm.mole-sec. Thus, since it is calculated by

\[
k_{13} = \frac{rC_6}{[iC_7^-][iC_4^+X^-]} \quad 2-3.13
\]

It is being calculated from \( rC_6 \) which is a measure of the rate of reaction 2-1.8. Thus, since it should be calculated from the rate of consumption of \( iC_7^- \) which could not be measured readily, the values would not necessarily follow the prediction.

The experimental value of \( k_{14} \) was about 45% lower than the predicted value. The reaction with which it is associated is

\[
iC_5^- + HX + k_{14} \rightarrow C_5^+X^- \quad 2-1.11
\]
It will be remembered that $k_1$ was also low. Obviously this implies that too high a value of $[iC_5^\equiv]$ was used in calculation of $k_{14}$.

The values of $k_{15}$ and $k_{16}$ are both about 300% higher than their respective predicted values. The reactions involved are

\[
\begin{align*}
 iC_7^+X^- + C_3^\equiv & \xrightarrow{k_{15}} C_{10}^+X^- & \quad 2-1.13) \\
iC_5^\equiv + iC_4^+X^- & \xrightarrow{k_{16}} C_9^+X^- & \quad 2-1.15)
\end{align*}
\]

Of course, this results in high rates of formation of $C_9$ and $C_{10}$. Since both the actual olefin concentrations involved have been shown to be low, the ions in the above reactions must have abnormally high concentrations. Of course, for this to be true, the reactions

\[
\begin{align*}
 iC_7^+X^- & \xrightarrow{k_{12}} iC_7^\equiv + HX & \quad 2-1.8) \\
iC_4^+X^- & \xrightarrow{k_9} iC_4^\equiv + HX & \quad 2-1.5)
\end{align*}
\]

must actually be affected very adversely by low temperature, as high concentrations of the ions would make these rates high. It is possible that a more active catalyst is needed to support the above reactions at low temperatures, e.g., 65°F.

To be general, the primary difference in the results obtained at 65°F. is the existence of abnormally high rates of $C_9$ and $C_{10}$.
The following reactions appear to be responsible for the high rates of formation of \( C_9 \) and \( C_{10} \), as the rate constants of these reactions are significantly higher than the predictions.

\[
\begin{align*}
iC_4^+X^- + C_3 &= \overset{k_{11}}{\longrightarrow} iC_7^+X^- \quad 2-1.3) \\
iC_7^+X^- + C_3 &= \overset{k_{15}}{\longrightarrow} C_{10}^+X^- \quad 2-1.13) \\
iC_5^+ + iC_4^+X^- &= \overset{k_{16}}{\longrightarrow} C_9^+X^- \quad 2-1.15)
\end{align*}
\]

Since the actual concentrations of the olefins which existed have been established in previous paragraphs to be, if anything, lower than predictions, the concentrations of the ions must be the cause of the higher rates. An unusually high concentration of \( iC_4^+X^- \) would contribute to a high concentration of \( iC_7^+X^- \) and \( C_9^+X^- \) by reaction 2-1.3 and 2-1.15 respectively. The high concentration of \( iC_7^+X^- \) would be responsible for the high concentration of \( C_{10}^+X^- \) by reaction 2-1.13. The \( C_7^-, C_9 \) and \( C_{10}^+ \) ions are, of course, the precursors of the \( C_7, C_9, \) and \( C_{10} \) saturates.

Thus, a possible explanation of the large values of \( k_{11}, k_{15} \) and \( k_{16} \) at 65°F. would be the existence of relatively large values of \( iC_4^+X^- \) at this temperature as compared to higher temperatures. This would explain also the apparent existence of low concentrations (as compared to predictions) of the olefins involved - they would be
consumed rapidly by the relatively higher rates of reaction for reactions 2-1.3, 2-1.13, and 2-1.15.

Why a lower temperature would cause a significant difference in the amount of tertiary-butyl cations present is speculative. The generation mechanism which was considered to be the source of these cations at other temperatures, i.e.,

\[
C_3^{=} + HX \xrightarrow{k_1} C_3^+X^- \quad 2-1.1)
\]

\[
C_3^+X^- + iC_4 \xrightarrow{k_2} C_3 + iC_4^+X^- \quad 2-1.2)
\]

must be ruled out due to the low yield of propane. One possible explanation would be that the low temperature acts as a stabilizing influence on the ions. This could allow the ions to build up to a large concentration just after startup when the hydrocarbon consists of almost entirely isobutane. Then, as the amount of \( C_3^{=} \) builds up within the reactor, reactions 2-1.3, 2-1.13, and 2-1.15 would begin to predominate. The only source of these ions would be via the organic diluents present in the acid. These diluents, present in about 2 to 3% by volume initially in "95%" acid were due to the 2,2,4-trimethylpentene added to the acid to simulate an alkylate catalyst. In the catalyst phase these diluents are thought to exist as trimethylpentenyl cations (8).
Even though these cations are considered quite stable and not reactive (8), there is the possibility that under conditions of high concentration of isobutane and high catalyst activity that the following hydride transfer reaction would occur.

\[
\text{At higher temperatures (e.g., 81°F. and above) the cyclopentenyl cation may be so much more stable than the tertiary-butyl cation that reaction 4-9 would not occur.}
\]

Another possible explanation for the large yields of C_9 and C_{10} is a change in mechanism at this temperature for the formation of these components. The reaction

\[
\text{C}_6^+X^- + C_3^= \xrightarrow{k_{17}} \text{C}_9^+X^-  \quad 2-1.16
\]

could become quite significant at lower temperatures. The low yield of propane would be explained by this as the other reaction which forms C_9, 2-1.15, requires formation of propane and 2-1.16 does not.

The explanation for high C_{10} formation could then be

\[
i\text{C}_5^+X^- + i\text{C}_5^= \rightarrow \text{C}_{10}^+X^-  \quad 4-10
\]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
section of this chapter since they are independent of catalyst concentration.

In Figure 4-19 the comparison of catalyst concentration effects on \( k_1 \) are shown where

\[
k_1 = \frac{rC_3}{[C_3][HX]} \tag{2-3.1}
\]

As can be seen, the values at 81°F. and 105°F. agree quite well, as they should. However, the value at 65°F. is very high. Propane was formed in a relatively large quantity (2.40% by weight) in the 65°F. experiment. This was just the opposite effect noticed in the 65°F., 95% experiment.

The values of \( k_9 \) are shown in Figure 4-20. This rate constant is calculated by

\[
k_9 = \frac{r_iC_8}{[iC_4^+X^-]} \tag{2-3.9}
\]

and the reaction is

\[
iC_4^+X^- \xrightarrow{k_9} iC_4^- + HX \tag{2-1.6}
\]

The value for 105°F. is in good agreement, whereas the values for 65 and 81°F. are low. A possible explanation is that the low acid concentration hinders self-alkylation until the temperature is high enough to compensate for catalyst inability to support such a reaction.
Figure 4-19. The values of $k_1$ obtained at a catalyst strength of 90% H$_2$SO$_4$ compared with the least squares fit of the values obtained at 95% H$_2$SO$_4$. 

$$C_3^+ + HX \xrightarrow{k_1} C_3^+ X^-$$
Figure 4-20. The values of $k_9$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$. 

$k_9 \times 10^{-4}$

$(sec.^{-1})$

$1/T \times 10^3 \left(^oC^{-1}\right)$
The values for \( k_{10} \) and \( k_{13} \) at a 90% \( \text{H}_2\text{SO}_4 \) concentration are shown with the predicted values in Table 4-5. The experimental values were higher than predicted at 65°C, 81°F, and 105°F. However, as was shown in the previous section the reactions with which \( k_{10} \) and \( k_{13} \) are associated are very fast. This, it will be remembered, implied that \( k_{10} \) and \( k_{13} \) were calculated from rates of formation which expressed the rates of the reactions

\[
iC_4^+ X^- \xrightarrow{k_9} iC_4^- + HX \quad 2-1.5)
\]

\[
iC_7^+ X^- \xrightarrow{k_{12}} iC_7^- + HX \quad 2-1.8)
\]

rather than from the reactions

\[
iC_4^- + iC_4^+ X^- \xrightarrow{k_{10}} iC_8^+ X^- \quad 2-1.6)
\]

\[
iC_7^- + iC_4^+ X^- \xrightarrow{k_{13}} iC_5^- + C_6^+ X^- \quad 2-1.9)
\]

with which they are associated. Therefore, they would not be expected to agree with the predictions.

The values for \( k_{11} \) are shown in Figure 4-21. The reaction from which \( k_{11} \) arises is

\[
iC_4^+ X^- + C_3^- \rightarrow iC_7^+ X^- \quad 2-1.3)
\]
<table>
<thead>
<tr>
<th>Temperature °F.</th>
<th>Reaction Rate Constant $k_{10}$ or $k_{13}$ Predicted (cc./gm.mole-sec.)</th>
<th>Reaction Rate Constant $k_{10}$ or $k_{13}$ Experimental (cc./gm.mole-sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>$4.73 \times 10^{16}$</td>
<td>$8.40 \times 10^{16}$</td>
</tr>
<tr>
<td>81</td>
<td>$5.83 \times 10^{16}$</td>
<td>$9.11 \times 10^{16}$</td>
</tr>
<tr>
<td>120</td>
<td>$7.81 \times 10^{16}$</td>
<td>$1.07 \times 10^{17}$</td>
</tr>
<tr>
<td>65</td>
<td>$1.84 \times 10^{17}$</td>
<td>$4.77 \times 10^{17}$</td>
</tr>
<tr>
<td>81</td>
<td>$2.47 \times 10^{17}$</td>
<td>$3.71 \times 10^{17}$</td>
</tr>
<tr>
<td>120</td>
<td>$3.72 \times 10^{17}$</td>
<td>$4.41 \times 10^{17}$</td>
</tr>
</tbody>
</table>

TABLE 4-5

The Predicted Values of $k_{10}$ and $k_{13}$ Compared to the Values Experimentally Determined Using a 90% $H_2SO_4$ Catalyst

$iC_4^+ + iC_4^- \overset{k_{10}}{\rightarrow} iC_8^+X^-$  

$iC_7^- + iC_4^+X^- \overset{k_{13}}{\rightarrow} iC_5^+ + C_6^+X^-$
Figure 4-21. The values of $k_{11}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$. 
The values for all three temperatures are higher and form a line approximately parallel to the 95% predictions. This was due mainly to the heavy products \( C_9 \) and \( C_{10} \) formed via the heptyl ion, which were high (Table 4-4) in relation to the feed olefin concentration (12.5%). Run Number One, \( 81^\circ F \), and 90% acid, resulted in the particularly high formation of \( C_9 \) (0.92% by weight) and \( C_{10} \) (3.84% by weight). It appears that the more dilute catalyst improves selectivity to the reaction of the type

\[
\text{ion} + \text{olefin} \rightarrow \text{ion}
\]

to the expense of the reactions of the form

\[
\text{ion} \rightarrow \text{olefin} + \text{proton}
\]

This does serve to increase the yield of \( C_7 \) products, also. This is supported by the fact that \( k_{12} \), Figure 4-22, from the reaction

\[
\text{iC}_7 + X^- \xrightarrow{k_{12}} \text{iC}_7 = + \text{HX} \quad \text{2-1.8)
\]

is consistently lower with a 90% acid concentration for \( 65^\circ F \), \( 81^\circ F \) and \( 105^\circ F \). The values for \( k_9 \) as just previously discussed are from a reaction of the same type and were also generally lower than those for the 95% catalyst.

The comparison for \( k_{14} \) is shown in Figure 4-23. The 90%
Figure 4-22. The values of $k_{12}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$. 

$$iC_7^++X^- \xrightarrow{k_{12}} iC_7^- + HX$$
Figure 4-23. The values of $k_{14}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$. 
values at 65°F. and 105°F. exhibit good to fair agreement with the 95% predictions. That for 81°F. is far below the prediction. This rate constant describes the kinetics of the following reaction:

\[ \text{iC}_5^- + \text{HX} \xrightarrow{k_{14}} \text{iC}_5^+X^- \quad 2-1.10 \]

Just why it should be low for this temperature, and not 65°F. and 105°F. also, is not obvious. The value of \( k_{14} \) is calculated by equation 2-2.15, and this disparity is probably caused by the combined errors in the measurement of the concentrations of \( \text{iC}_5^- \), \( \text{C}_6^- \), and \( \text{C}_9^- \), all of which had concentrations less than 1%.

Figures 4-24 and 4-25 show the effects of catalyst strength on \( k_{15} \) and \( k_{16} \) respectively. These rate constants relate the rates of \( \text{C}_9^- \) and \( \text{C}_{10}^- \) formation. The reactions are

\[ \text{iC}_7^+X^- + \text{C}_3^- \xrightarrow{k_{15}} \text{C}_{10}^+X^- \quad 2-1.13 \]

\[ \text{iC}_5^- + \text{iC}_4^+X^- \xrightarrow{k_{16}} \text{C}_9^+X^- \quad 2-1.15 \]

Reflecting the high rates of formation (see Table 4-4) of \( \text{C}_9^- \) and \( \text{C}_{10}^- \) for a 90% catalyst strength, \( k_{15} \) and \( k_{16} \) are higher than the prediction for all three temperatures. The value for 105°F. is lower than those for 65°F. and 81°F., suggesting an apparent increase in selectivity at this temperature to the primary product - i.e., dimethylpentanes.
Figure 4-24. The values of $k_{15}$ obtained at a catalyst strength of 90% $\text{H}_2\text{SO}_4$ compared with the least squares fit of the values obtained at 95% $\text{H}_2\text{SO}_4$. 

\[ i\text{C}_7^+X^- + \text{C}_3 = \frac{k_{15}}{1/T \times 10^3 \, (\text{oR}^{-1})} \rightarrow \text{C}_{10}^+X^- \]
Figure 4-25. The values of $k_{16}$ obtained at a catalyst strength of 90% $\text{H}_2\text{SO}_4$ compared with the least squares fit of the values obtained at 95% $\text{H}_2\text{SO}_4$. 
The 90% catalyst concentration results for $k_{18}$ as compared to the 95% correlation appear in Figure 4-26. While the 65°F. value is in good agreement, the values for 81°F. and 105°F. are low. $k_{18}$ results from the following reaction:

$$C_{10}^{+}X^{-} \xrightarrow{k_{18}} iC_{5}^{=} + iC_{5}^{+}X^{-} \quad 2-1.18)$$

These low values are in agreement with those of $k_{12}$ which is reflected in the overall sequence.

$$iC_{7}^{=} + iC_{4}^{+}X^{-} \xrightarrow{k_{13}} iC_{5}^{=} + C_{6}^{+}X^{-} \quad 2-1.9)$$

Since $iC_{7}^{=}$ appears in no other reaction and $k_{13}$ is $\gg k_{12}$, the implication is

$$iC_{7}^{+}X^{-} \xrightarrow{k_{12}} iC_{5}^{=} + C_{6}^{+}X^{-} \quad 4-22)$$

which allows comparison between $k_{12}$ and $k_{18}$, showing that the rate of cracking of a carbonium ion is lower at 90% than at 95% $H_{2}SO_{4}$.

The consequence of low values for $k_{12}$ and $k_{18}$ was, of course, high yields of $C_{10}$ at the expense of the more desirable lighter products $C_{5}$ through $C_{7}$.

In general, the main effect of the low catalyst concentration
Figure 4-26. The values of $k_{18}$ obtained at a catalyst strength of 90% $H_2SO_4$ compared with the least squares fit of the values obtained at 95% $H_2SO_4$. 
was to increase product ions of C₉ and C₁₀, at the expense of lighter products. The iC₈ formation at lower temperatures - 65 to 81°F. - was also low; however, it increased to the same value which would be predicted at 95% H₂SO₄ and 105°F.

As can be seen from Table 4-4, the effect of increasing temperature to 105°F. results in a far superior product, i.e., the increased yields of the desirable iC₇ and iC₈ and the decreased yields of C₉ and C₁₀. It appears that this higher temperature makes up for loss in selectivity of the dilute catalyst. There were two investigations reported in the literature on the effect of catalysts concentration on olefin-isobutane alkylation with sulfuric acid catalyst. These were by Shlegeris (30), who alkylated propene, and Mosby (23), who alkylated butene-1. Shlegeris (30) used a 95.5% catalyst obtained from an American Oil Company commercial alkylation unit for comparison with the results he obtained at 99.3%. The only comparison he gave was that conversion decreased with the lower strength catalyst. This could be the reason why his conversions only reported at 99.3% H₂SO₄ appear high in relation to this work. The decrease in conversion with acid strength was not noted in this work; however, the 95% and 90% catalysts used in this work both had the same character. However, the 99.3% and 95.5% catalysts Shlegeris used did not. The larger amount of organic diluents in this work may have actually aided conversion by promoting the solubility of isobutane more than the corresponding loss of activity upon dilution.
Mosby (23) investigated the effect of acid concentration on the alkylation of isobutane with butene-1. The acid he used was made by blending a used alkylation catalyst similar to that used by Shlegeris with fuming $\text{H}_2\text{SO}_4$. Though the olefin was different, some qualitative comparisons can be made.

Mosby found that as in this work the "C<sub>9</sub> plus" fraction of the product was higher at a concentration of 90-91% than at 94-95%. He also found that the product fraction of C<sub>5</sub> through C<sub>7</sub> - comparable to C<sub>5</sub> and C<sub>6</sub> in this work - decreased with decrease in acid strength. Similar results were noted in this work. His primary product, octanes, decreased with decreasing acid strength from 94 to 90%. The fact that the octanes in this work also decreased, even though they were formed by self-alkylation rather than direct alkylation, is interesting. The fraction of the primary product, heptane, remained more or less constant on the average of about 55% in this work with change in catalyst strength.

VI. Other Related Research

There have been other alkylation studies reported in the literature, but for various reasons, as will be discussed, it is not possible to make a comparison of the results of these studies with those of this research. In general, only qualitative information is reported. For example, in the work of Jernigan, Gwyn, and Claridge (14) a typical refinery feed containing mixed butenes, propylene, pentenes,
and C₃ to C₅ paraffins was used. The reaction temperature was typical for butene alkylation, 45°F. The acid concentrations varied from 98 to 86% H₂SO₄ in acid depletion experiments with a vertical, draft-tube alkylation reactor using a contactor speed of 3,000 to 3,600 RPM. This was mainly a study to characterize the hydrocarbon acid emulsion which was varied from 14 to 68% H₂SO₄ in the emulsion. The ratio of C₈ to other C₆ plus by volume was reported to vary from 0.44 to 2.26. It was not possible to make any worthwhile comparisons between this work and our research.

Next, Knoble and Hebert's commercial scale work (17) involved the alkylation of isobutane with propylene, the data which was reported being strictly commercial in application. There were no product analyses other than ASTM 90% distillation point, end point and octane number; thus, no comparisons can be made. This work was reviewed in detail in Chapter I.

In a survey article by Cupit, Gwyn and Jernigan (7) data was presented which included the results from isobutane-propylene alkylation. This data was obtained at 46°F., a catalyst concentration of 98%, 47% acid in emulsion, and a 0.22 olefin space velocity. However, the concentration of propane was not reported, and the feed contained 15.9% (vol.) propylene, 77% (vol.) isobutane, and 7.1% (vol.) normal paraffins.

Due to the low temperature used, 46°F., the low value of
acid in emulsion, 47% (vol.), and the fact that only one piece of data was reported, these results can only be used qualitatively as a comparison to our research. A comparison of these results with the data from this research which is closest to their operating conditions is shown in Table 4-6.

It will be noted in the data of Cupit et al. that the $C_3 - nC_5$ actually decreased from the feed to the product. As propane is generally formed in these reactions and normal paraffins are generally inert to alkylation, this would indicate that there were inaccuracies in the chemical analysis. Therefore, only the relative magnitudes of the composition should be considered. It is quite probable, also, that the olefin used was not pure propylene, as pure propylene alkylation requires either very high acid concentration (4) (>100% $H_2SO_4$) and/or higher temperatures (31) (e.g., >55-60°F. range) to obtain yields in the range of that reported in the survey article. The impurities in the olefin were probably butenes. The fact that butenes are good promoters of propylene alkylation (17) would explain the higher yields of heptanes and lower yields of $C_9$ and $C_{10}$ than were obtained in Experiment Nine. The relatively high yields of heptanes may also be the result of the shorter contact time obviously employed in obtaining the data presented in the survey article, as in the same article it was stated that "short contact times" favor the primary reactions.
### TABLE 4-6
Comparison of Alkylation Data from Cupit et al. (7)* with That of Experiment Nine

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Cupit et al.</th>
<th>Nine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Strength (% H₂SO₄)</td>
<td>98</td>
<td>95</td>
</tr>
<tr>
<td>Olefin Space Velocity (hr.⁻¹)</td>
<td>0.22</td>
<td>0.118</td>
</tr>
<tr>
<td>Temperature (°F.)</td>
<td>46</td>
<td>65</td>
</tr>
<tr>
<td>Acid in Emulsion (Vol. %)</td>
<td>47</td>
<td>60</td>
</tr>
<tr>
<td>Feed Composition (Wt. %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃=</td>
<td>14.9</td>
<td>14.3</td>
</tr>
<tr>
<td>iC₄</td>
<td>77.7</td>
<td>85.7</td>
</tr>
<tr>
<td>C₃ - nC₅</td>
<td>7.4</td>
<td>Trace</td>
</tr>
<tr>
<td>Product Composition (Wt. %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iC₄</td>
<td>58.6</td>
<td>69.83</td>
</tr>
<tr>
<td>C₃ - nC₅</td>
<td>6.8</td>
<td>1.59**</td>
</tr>
<tr>
<td>iC₅</td>
<td>1.0</td>
<td>0.97</td>
</tr>
<tr>
<td>2,3-DMB and MP</td>
<td>1.2</td>
<td>1.24</td>
</tr>
<tr>
<td>2,4-DMP</td>
<td>6.1</td>
<td>5.24</td>
</tr>
<tr>
<td>2,3-DMP</td>
<td>15.4</td>
<td>11.05***</td>
</tr>
<tr>
<td>Total C₇</td>
<td>21.5</td>
<td>16.29</td>
</tr>
<tr>
<td>2,4,4-TMP</td>
<td>1.4</td>
<td>1.38</td>
</tr>
<tr>
<td>2,3,3- and 2,3,4-TMP</td>
<td>1.1</td>
<td>1.15</td>
</tr>
<tr>
<td>DMC₆ and Other C₈</td>
<td>0.5</td>
<td>1.75</td>
</tr>
<tr>
<td>Total C₈</td>
<td>3.0</td>
<td>4.28</td>
</tr>
<tr>
<td>2,2,5-TMC₆</td>
<td>0.3</td>
<td>0.46</td>
</tr>
<tr>
<td>Other C₉</td>
<td>0.1</td>
<td>0.91</td>
</tr>
<tr>
<td>Total C₉</td>
<td>0.4</td>
<td>1.37</td>
</tr>
<tr>
<td>C₁₀</td>
<td>1.7</td>
<td>4.43</td>
</tr>
<tr>
<td>C₁₁</td>
<td>1.2</td>
<td>(&lt;1)</td>
</tr>
</tbody>
</table>

* This data has been converted from a volume percent basis to a weight percent basis; therefore, there are fewer significant figures.

** Propane

*** Includes 3MC₆
VII. Conclusions

According to the results found in this work, the mathematical model derived in Chapter II is valid over the temperature range of 81°F. to 135°F. for the alkylation of isobutane with propylene using a 95% by weight sulfuric acid catalyst. In this range of temperatures the rate of formation of each species except iC₅ is adequately explained by one reaction path. The iC₅ species requires two reaction paths as discussed in Chapter II. Thus, this type of model may be used to analyze the data from complex, liquid-liquid reactions. This presupposes, however, that an accurate description of the reaction mechanism is known.

A regression model from the experimentally determined rate constants indicates the following trends in the range of 81°F. to 135°F.

1. Yield increases both with temperature and olefin feed concentration.

2. The weight fraction of iC₇ is insensitive to temperature changes but increases with increase in olefin feed concentration.

3. The octane concentration decreases with increase of both temperature and olefin feed concentration.

4. The propane concentration remains constant with temperature but decreases with increasing olefin feed concentration.

5. The product fractions of C₅, C₆, C₉ and C₁₀ all increase with increasing olefin feed concentration.
6. Based on the first five trends, low temperatures (down to 81°F.) and low olefin feed concentrations (down to 12.5%) give the highest concentration of the desired products, C7 and C8, and lowest concentrations of the undesirables, C9 and C10.

For a 95% catalyst concentration, this research shows a change in the mechanism, and thus the product distribution, at 65°F. This is thought due to either a significant departure in the rate of formation of tertiary-butyl cations or to a change in reaction path. This difference in mechanism causes primarily a large increase in the C9 and C10 concentrations.

Low acid concentrations, e.g., 90%, yield high concentrations of C9 and C10. The high C9 and C10 yields were considered to be a consequence of a change in selectivity to these products. In addition, since C7 yields were comparable to the yields at 95% H2SO4, the increased amount of organic diluents present in the catalyst probable aided conversion since isobutane solubility is thought to be enhanced with increased organic diluent.

VIII. Recommendations

In any program of research, the immediate goals are usually attained. The valuable by-products of such a program, however, will surely include new questions which arise during the course of the work. Consequently, there are always many recommendations which arise from these investigations. The recommendations
here will be in line with problems which arose during the course of this study. These recommendations are presented in the following list.

1. Solubilities of the various isoparaffins in sulfuric acid are needed as both a function of temperature and percent $\text{H}_2\text{SO}_4$ (organically diluted).

2. Since the results obtained from the mathematical model are dependent to some extent on the olefin feed concentration, a more detailed study of this variable is needed. Specifically, the assumption that the concentrations of the feed olefin in both phases are related by a simple proportion may be a limitation of this model. It is suggested that experiments be designed and carried out to determine a more exact functional relationship between the olefin concentration in the feed and that in the acid.

3. More study is needed to determine what the change in mechanism is upon going from $81^\circ\text{F}$ to $65^\circ\text{F}$.

4. As most commercial alkylation units do not have the degree of mixing which the one used in this work had, the results from this work may not be directly applicable due to mixing effects. Thus, it is recommended that a study of the effect of mixing on the alkylation reactions. Thus, this kinetic model may be extended to include other reactions which may become significant at lower degrees of mixing.
NOMENCLATURE

\[ A = \text{mass transfer area per unit volume of emulsion} - \text{ft.}^2/\text{ft.}^3 \]
\[ A_i = \text{area of peak } i \text{ on chromatogram} \]
\[ C = \text{concentration of tracer at time } t - \text{counts/min.} \]
\[ C_0 = \text{initial concentration of tracer} - \text{counts/min.} \]
\[ C_i = \text{saturated hydrocarbon of carbon number } i \]
\[ C_i^z = \text{monounsaturate of carbon number } i \]
\[ C_i^+ = \text{carbonium ion of carbon number } i \]
\[ C_i^\infty = \text{weight concentration of species } C_i \]
\[ d = \text{fraction of dead space in reactor} \]
\[ E = \text{activation energy} - \text{Kcal./gm. mole} \]
\[ F_{C_i} = \text{molal feed rate of component } C_i \text{ per unit volume of acid in reactor} - \text{moles/(hr.-ft.}^3) \]
\[ H = \text{volume fraction of acid in reactor} \]
\[ H_{e} = \text{volume fraction of hydrocarbon in reactor which is emulsified} \]
\[ k_i = \text{reaction rate constant} - \text{sec.}^{-1} \text{ or cc./gm.mole-sec.} \]
\[ k_m = \text{mass transfer coefficient} - \text{ft./hr.} \]
\[ K_m = \text{mass transfer coefficient} - \text{lb./(hr.-ft.}^2) \]
\[ K_{D1}, K_{D_i} = \text{phase distribution coefficients} \]
\[ K_I = \text{fraction of carbonium ions which are not } C_4 \text{ carbonium ions} \]
\[ m = \text{fraction of reactor contents which are perfectly mixed} \]
\[ M = \text{molecular weight} \]
\[ N_i = \text{total mass transfer of species } i - \text{lb./hr.} \]
\[ p = \text{fraction of reactor contents which are in a plug flow region} \]
\[ P_i = \text{product rate of species } i \text{ per unit volume of catalyst - lb. mole/(hr. - ft.}^3) \]
\[ r_{C_i} = \text{rate of formation of species } C_i \text{ per unit volume of catalyst - lb. mole/(ft.}^3\text{-hr.}) \]
\[ R = \text{gas constant } 1.987 \text{ Btu/(lb. mole - } ^\circ \text{R}) \]
\[ S = \text{olefin space velocity - vol. olefin/vol. acid-hr.} \]
\[ t_R = \text{mean residence time of reactor - minutes} \]
\[ w = \text{constant in reaction rate constant temperature dependence expression} \]
\[ W = \text{mass flow rate - lb./hr.} \]
\[ W_p = \text{weight percent} \]
\[ X = \text{fraction of } C_9 \text{ formed via } iC_5 = \]
\[ X^- = HSO_4^- \]
\[ Y_{C_i} = \text{mole fraction of component } C_i \text{ in acid phase based on saturated reaction products only} \]
\[ Z = \text{constant of proportionality between concentration of } C_i \text{ and } C_i + X^-; \text{ equal to } 10^{-8} \text{ for propane, } 10^{-7} \text{ for other species} \]
\[ [C_i] = \text{concentration in acid phase of species } C_i - \text{lb. moles/ft.}^3 \]

**Subscripts:**

- acid = acid phase
- HC = hydrocarbon phase

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
m, n, i = number of carbon atoms in a species

R = reactor or reaction

Superscript:

* = implies equilibrium value

Greek letters:

α = proportionality

ρ = density - lb./ft.³

Σ = summation

θ = dimensionless time

Numerical subscripts in computer program as applied to hydrocarbon species

1 = C₄ species
2 = C₃ species
3 = C₅ species
4 = C₆ species
5 = C₇ species
6 = C₈ species
7 = C₉ species
8 = C₁₀ species
BIBLIOGRAPHY


30. Shlegeris, R. J., copy of a manuscript obtained from Industrial and Engineering Chemistry, September 1968.


APPENDIX A

ELIMINATION OF REACTION INTERMEDIATES

The standard procedure in the determination of rate constants for a set of complex reactions where reaction intermediates are involved is to eliminate the intermediate through steady state approximations (18). The resulting kinetic model generally involves ratios of rate constants. In many cases values for one or more of the individual rate constants may be determined which then may be used to determine the values of the other rate constants. In this case, however, if the intermediates are eliminated, there is no way to determine the individual values of any rate constant except $k_1$. This is shown in the derivation on the following pages. Also, ratios of rate constants do not allow a valid test of a model on an Arrhenius plot, as, of course, only relative temperature effects are noticed. Thus, since the Arrhenius correlation was the basis of determining the validity of the model, it was decided that the concentrations of the intermediates be estimated rather than eliminated.

The "knowns" in the mathematical model (equations 2-3.1 through 2-3.18) are $r_{C_3}$, $r_{C_5}$, $r_{C_7}$, $r_{C_8}$, $r_{C_9}$, $r_{C_{10}}$, $[HX][C_3]^z$, and $[iC_4]$. The last two quantities must be estimated.

Therefore:

$$k_1 = \frac{r_{C_3}}{[C_3]^z[HX]}$$  

2-3.1)
Substituting this into equation 2-3.11,

\[
\frac{k_{11}}{k_9} = \frac{r_{C_7} + r_{C_{10}} + (r_{C_5} + r_{C_6} + r_{C_9})/2}{[C_3^+]r_{C_8}} \tag{A-1}
\]

\[
[iC_7^+] = \frac{r_{C_6} + (1 - x)r_{C_9}}{k_{12}} \tag{2-3.12}
\]

\[
[iC_7^+] = \frac{r_{C_7}}{k_5[iC_4]} \tag{2-3.5}
\]

Equating 2-3.12 to 2-3.5,

\[
\frac{k_{12}}{k_5} = \frac{r_{C_6} + (1 - x)r_{C_9}}{r_{C_7}/[iC_4]} \tag{A-2}
\]

\[
[iC_5^+] = \frac{r_{iC_5} + r_{C_6} - (2x - 1)r_{C_9}}{2[HX]k_{14}} \tag{2-3.14}
\]

Substituting 2-3.9 and 2-3.14 into 2-3.16,

\[
\frac{k_{16}}{k_{14}k_9} = \frac{2xr_{C_9}[HX]}{\left\{r_{iC_5} + r_{C_6} - (2x - 1)r_{C_9}\right\}r_{C_8}} \tag{A-3}
\]

Substituting 2-3.12 into 2-3.15,
\[
\frac{k_{15}}{k_{12}} = \frac{r_{C_5} - r_{C_6} + (2x - 1)r_{C_9} + 2r_{C_{10}}}{2[C_3^+] \left\{ r_{C_6} + (1 - x)r_{C_9} \right\}} \quad \text{A-4)}
\]

Now,
\[
[C_6^+X^-] = \frac{r_{C_6}}{k_4[iC_4]} \quad \text{2-3.4)}
\]

Substituting 2-3.4 into 2-3.17,
\[
\frac{k_{17}}{k_4} = \frac{(1 - x)r_{C_9}[iC_4]}{r_{C_6}} \quad \text{A-5)}
\]

\[
[C_{10}^+X^-] = \frac{r_{C_{10}}}{k_8[iC_4]} \quad \text{2-3.8)}
\]

Substituting 2-3.8 into 2-3.18,
\[
\frac{k_{18}}{k_8} = \frac{r_{C_5} - r_{C_6} + (2x - 1)r_{C_9}}{r_{C_{10}}/[iC_4]} \quad \text{A-6)}
\]

There are no substitutions for $[C_3^+X^-]$, $[C_5^+X^-]$, $[C_8^+X^-]$, $[C_9^+X^-]$, $[iC_4^+]$, and $[iC_7^+]$,

and
\[
k_2 = \frac{r_{C_3}}{[C_3^+X^-][iC_4^+]} \quad \text{2-3.2)}
\]
\[ k_3 = \frac{r_{C_5}}{[C_5^+X^-][iC_4]} \]  \hspace{1cm} 2-3.3)

\[ k_6 = \frac{r_{C_8}}{[C_8^+X^-][iC_4]} \]  \hspace{1cm} 2-3.6)

\[ k_7 = \frac{r_{C_9}}{[C_9^+X^-][iC_4]} \]  \hspace{1cm} 2-3.7)

\[ k_{10} = \frac{r_{C_8}}{[iC_4^=][iC_4^+] \]  \hspace{1cm} 2-3.10)

Substituting 2-3.9 into 2-3.10,

\[ \frac{k_{10}}{k_9} = \frac{1}{[iC_4^=]} = \text{unknown} \]  \hspace{1cm} A-7)

Substituting 2-3.9 into 2-3.13,

\[ \frac{k_{13}}{k_9} = \frac{r_{C_6} + (1 - x)r_{C_9}}{[iC_7^{=}]r_{C_8}} = \text{unknown} \]  \hspace{1cm} A-8)

Thus, constants \( k_2, k_3, k_6, k_7, k_{10} \) and \( k_{13} \) may not be evaluated. \( k_1 \) may be evaluated but it does not appear in any of the ratios A-1 through A-8.

The ratios A-1 through A-8 may be algebraically manipulated, but the only results would be to obtain other ratios and,
thus, the rate constants $k_{11}$, $k_{12}$ and $k_{14} - k_{18}$ cannot be determined individually.
APPENDIX B

CALCULATION OF RATE CONSTANTS

Using equations 2-3.1 through 2-3.18 the values for the eighteen rate constants may be calculated for any one experiment.

A computer program has been written for this purpose. The program, entitled EX - for experimental, requires the following inputs:

1. Component weight percent directly from each chromatogram - WHC(I)
2. Component molecular weights - CMW(I)
3. Component liquid densities (20) - DENS(I)
4. Mass transfer coefficient - CMT(I)
5. Volumetric ratio of propylene to isobutane in the feed - R
6. The volume fraction of acid in the reactor - ACID
7. The volumetric feed rate - CCI
8. The volumetric product rate - CCO
9. The reaction temperature - TEMP
10. The reaction pressure - PRESS
11. The final density of the catalyst used (26) - DENS(A)
12. The value for the proportion between the ions and saturates - Z

The output of the program includes the following:

1. TEMP
2. PRESS
(3) $R$

(4) The olefin space velocity - $S$

(5) ACID

(6) The molar concentration of the catalyst - $ACIDC$

(7) The mean residence time - TR

(8) The molar rate of propylene fed - PROP M

(9) The molar rate of isobutane fed - BUTM

(10) The product molar rate - SUMM

(11) The mass rate of feed in - TOTW

(12) The mass rate of product - WTIN

(13) The weighted inverse density of the product - SUMW

(14) WHC(I)

(15) The component product weight flows - CWP(I)

(16) The component product molar flows - CMP(I)

(17) The component weight concentration in the acid phase - CONWA(I)

(18) The component molar concentrations in the acid phase - CONCA(I)

(19) The molar concentrations of the olefins in the acid phase - COLE(I)

(20) The molar concentrations of the ions in the acid phase - CION(I)

(21) The values for the rate constants - RK(J)

The rate constants from the experiments run at conditions between 81 and $135^\circ F.$ and 95% $H_2SO_4$ were used as inputs to MRP
49 - the General Foods Multiple Regression Program. This program converted the input rate constants to logarithms and made a least squares fit of the log k versus inverse temperature. The results were in the form of the slope and intercept of the best straight line fit of the log k versus inverse temperature plot.

The output from MRP 49 was put unchanged into the program, PR - for prediction. The inputs were

(1) The logarithm of the least squares intercept - RKOL(I)
(2) The least squares slope - SL(I)

The output was

(1) The predicted value of the rate constants at the following temperatures:
   (a) 65°F. - RKJ(I)
   (b) 81°F. - RKL(I)
   (c) 105°F. - RKM(I)
   (d) 120°F. - RKN(I)
   (e) 135°F. - RKH(I)

(2) The frequency factor - RKO(I)

(3) The natural logarithmic base slope - SLN(I)

(4) The activation energy - ACTE(I)

The flow diagrams and corresponding print-outs for EX and PR are given on the following pages.
FLOW DIAGRAM
OF COMPUTER PROGRAM EX

Start

I = 0
L = 0

Read number of analyses, M

L = L + 1

Read number of components, N

I = I + 1

Read subscripted data; DATA(I), (WHC(I), CMW(I), DENS(I), CMT(I))

SUM(L, I) = DATA(I)

No

I = N

Yes
Read data; R, ACID, CCI, CCO, TEMP, PRESS, DENS, Z

Convert acid density, DENS, to concentration, ACIDC

Convert cc./min. (CCI, CCO) to ft.³/hr. (VFR, VPR)

Calculate weight flow of product for material balance;

\[ \text{WTIN} = \frac{\text{VPR}}{\text{WHC(I)/DENS(I)}} \]

Calculate weight flow of feed; TOTW =

\[ \text{TOTW} = (R/R+1 \times 32.54 + 35.08/R+1) + \text{VFR} \]

I = 0

I = I + 1

Calculate component weight flows;
\[ \text{CWP(I)} = \frac{\text{TOTW}}{\text{WHC(I)}} \]

Calculate component molar flows/volume of catalyst;
\[ \text{CMP(I)} = \frac{\text{CMW(I)}}{0.0347} \]
No

I = N

Yes

Calculate molar product rate;

\[ \text{SUMM} = \text{CMP}(I) \]

Calculate \( C_3 \) and \( iC_4 \) molar feed rates/volume of catalyst;

\[ \text{PROPm} = \frac{VFR}{R + 1} \frac{32.54}{42.1 \times 0.0347} \]

\[ \text{BUTM} = \frac{VFR}{R + 1} \frac{35.08}{58.1 \times 0.0347} \]

Calculate residence time of hydrocarbon;

\[ \text{TR} = 0.0579 \left( 1.0 - \text{ACID} \right) / VFR \]

I = 0

I = I + 1

Calculate solubilities of product components;

\[ \text{SW}(I) = \frac{58.1}{\text{CMW}(I) \times 0.001} \]
Calculate component weight concentrations (lb./lb.) in the acid phase; CONWA(I) by mass transfer equation 2-16 using

\[ K_{D_i} = \frac{1}{SW(i)} \]

Calculate acid phase molar concentrations (lb. mole/ft.³);

\[ CONCA(I) = \frac{CONWA(I) \times DENS\text{A}}{CMW(I)} \]

Set isobutane weight concentration; CONWA(1) = 0.007

Calculate \( C_3 \) concentration by equation 2-15; result is COLE(2)

Calculate \( iC_4 \), \( iC_5 \), and \( iC_n \) concentrations by equations 2-26, 2-27, and 2-28. Results are COLE(1), COLE(3), COLE(5)

Calculate rate constants by equations 2-3.1 - 2-3.18. Results are RK(J)
Convert RK(J) to metric system of units;

\[ \frac{\text{cc.}}{\text{gm. mole-sec.}} = \frac{\text{ft.}^3}{\text{lb. mole-hr.}} \times 1.739 \times 10^{-2} \]

\[ \text{sec.}^{-1} = \text{hr.}^{-1} \times 2.777 \times 10^{-4} \]

Print results, TEMP, PRESS, R, S, ACID, ACID, ACIDC, TR, PROP, BUTM, SUMM, TOTW, SUMW

\[ J = 0 \]

\[ J = J + 1 \]

Print RK(J)

No

\[ J = 18 \]

Yes

Stop
DIMENSION WHC(20),PDC(20),CMT(20),CWP(20),CMP(20),CMFHC(20),CONWA(20),CONCH(20),CONCA(20),COLE(20),CION(20),RK(20),DFNS(20),CMW(20),L,SM(20),SW(20),W(20,20),T(20,20),U(20,20),V(20,20)

DO73LL=1,9
I=1
L=1
W(L,I)=0.0
T(L,I)=0.0
U(L,I)=0.0
V(L,I)=0.0
A=0.0
B=0.0
C=0.0
D=0.0
READ4,M
4 FORMAT(6X,I6)
DO72L=1,M
11 READ12,N
12 FORMAT(6X,I6)
DO14I=1,N
READ13,J,WHC(I),CMW(I),DENS(I),CMT(I)
13 FORMAT(6X,I6,4F12.6)
W(L,I)=WHC(I)
T(L,I)=CMW(I)
U(L,I)=DENS(I)
V(L,I)=CMT(I)
14 CONTINUE
72 CONTINUE
DO900I=1,N
DO901L=1,M
A=A+U(L,I)
B=B+T(L,I)
C=C+U(L,I)
D=D+V(L,I)
901 CONTINUE
WHC(I)=A/M
CMW(I)=B/M
DENS(I)=C/M
CMT(I)=D/M
A=0.0
B=0.0
C=0.0
D=0.0
900 CONTINUE
READ17,R,ACID,CCI,CCO,TEMP,PRESS,DENSA,Z
17 FORMAT(6X,8F8.4)
Z=Z*1.0E-05
ACIDC=DENSA/98.1
IF(ACIDC-1.*155)500,501,501
500 ACIDC=ACIDC*0.90
GO TO 502
501 ACIDC=ACIDC*0.95
502 CONTINUE
VFR=CCI*(0.002118)
VPR=CCO*(0.002118)
SUMW=0.0
DU181=1,N
18 SUMW=SUMW+WHC(I)/DENS(I)
WTIN=VPR/SUMW
TOTW=VFR*(R/(R+1.0))*32.54+35.08/(R+1.0))
SUMM=0.0
DN191=1,N
CWP(I)=TOTW*WHC(I)
CMP(I)=CWP(I)/(CMW(I)*0.0347)
19 SUMM=SUMM+CMP(I)
PROPW=VFR*(R+1.0)*32.54
BUTW=VFR*(35.08/(R+1.0))
PROPM=PROPW/(42.1*0.0347)
BUTM=BUTW/(58.1*0.0347)
VHCR = 0.0579 * (1.0 - ACID)
TR = VHCR / VFR
S = (VFR * R / (R + 1.0)) / (ACID * 0.0579)
DO201 = 1, N
CMFC(1) = CMP(1) / SUMC
CMFC(9) = 0.0
20  CONCH(2) = WHC(1)
DO161 = 1, N
16  SW(1) = (58.1 / CMW(1)) * 0.001
CONWA(1) = 0.0007
CONCA(1) = CONWA(1) * DENS/cmw(1)
DO211 = 2, N
CONWA(1) = CONCH(1) * SW(1) + CMP(1) * SW(1) / (CMT(1) * 0.0579)
CONCA(1) = CONWA(1) * DENS/cmw(1)
21  COLE(1) = 0.00E-30
SUMC = 0.0
DO8001 = 2, 8
800  SUMC = SUMC + CONCA(1)
DO1001 = 1, N
100  CI(1) = CONCA(1) * 2
CI(1) = CI(1) * (R / (R + 1.0)) / (0.154 / 1.154)
CI(2) = CI(2) * 0.1
COLE(1) = CONCA(6) / SUMC * CI(1)
COLE(2) = 1.0E-09
COLE(1) = (R / (R + 1.0)) / (0.154 / 1.154) * COLE(2)
COLE(1) = (2.0 * CONCA(4) + CONCA(7)) / SUMC * CI(1)
COLE(3) = (CONCA(3) + CONCA(7)) / SUMC * (COLE(5) + CI(1))
X = 1.0
DO2001 = 2, N
200  RK(1) = CMP(1) / (CI(1) * CONCA(1))
RK(1) = CMP(2) / (COLE(2) * ACID)
RK(9) = CMP(6) / CI(1)
RK(10) = RK(9) / COLE(1)
RK(11) = (CMP(5) + CMP(8) + (CMP(3) + CMP(4) + CMP(7)) / 2.0) / (CI(1) * COLE(2)
1)
1       WTIN  )
   PRINT 40,TR,PROP,M,BUTM,SUMM,TOTW,SUMW,WTIN
40 FORMAT(1HO,F7.4,3F8.5,3F12.3)
   PRINT45
45 FORMAT(1H-,45H I WHC(I) CWP(I) CMP(I) CONCH(I))
   DO51I=1,N
   PRINT50,I,WHC(I),CWP(I),CMP(I),CONCH(I)
50 FORMAT(1HO,I3,F8.5,F12.6,F12.8,F10.6)
51 CONTINUE
   PRINT55
55 FORMAT(1H-,59H I CONWA(I) CONCA(I) COLE(I) C)
   LION(I) )
   DO61I=1,N
   PRINT 60,I,CONWA(I),CONCA(I),COLE(I),CION(I)
60 FORMAT(1HO,I3,E14.6)
61 CONTINUE
   PRINT65
65 FORMAT(1H-,23H J  RK(J) )
   DO71 J=1,18
   PRINT70,J,RK(J)
70 FORMAT(1HO,I3,E20.8)
71 CONTINUE
73 CONTINUE
400 STOP
   END
FLOW DIAGRAM
FOR COMPUTER PROGRAM PR

Start

I = 0

I = I + 1

Read data;
RKOL(I), SL(I)

Take antilog of RKOL(I) and convert to metric system;

\[
\text{cc/gm. mole-sec.} = \text{ft.}^3/\text{lb. mole} \\
\times 1.739 \times 10^{-2}
\]

\[
\text{sec.}^{-1} = \text{hr.}^{-1} \times 2.777 \times 10^{-4}
\]

No

I = 17

Yes

I = 0

I = I + 1
Convert SL(I) to natural logarithmic base; 
\[ SLN(I) = 2.30258 \times SL(I) \]

Calculate the activation energy ACTE(I) in metric units; 
\[ ACTE(I) = -1.987 \times SLN(I)/1.8 \]

Calculate the predicted values of the rate constants at 65°F, 81°F, 105°F, 120°F, and 135°F by equation 2-15; results are RKJ(I), RRL(I), RKM(I), RKN(I), and RKH(I)

\[
\text{No} \quad I = 17 \\
\text{Yes} \quad I = 0 \\
\quad I = I + 1 \\
\quad \text{Print RKJ(I), RKL(I), RKM(I), RKN(I), RKH(I)} \\
\text{No} \quad I = 17 \\
\text{Yes} \quad I = 0
\]
I = I + 1

Print RK0(I), SLN(I), ACTE(I), RKH(I), RKL(I)

No

I = 17

Yes

Stop
DIMENSION RKO(20), RKL(20), SL(20), ACTE(20), RKL(20), RCL(20) 
1, RKJ(20), RKM(20), RKN(20) 
DO 100 I=1,17 
READ20,J,RKOL(I),SL(I) 
20 FORMAT(6X,I6,2E14.8) 
RKO(I)=EXP(2.30258*RKOL(I))*1.739E-02 
100 CONTINUE 
BB=(2.7777E-02)/1.739 
RKO(I)=RKO(I) 
RKO(9)=RKO(9)*BB 
RKO(12)=RKO(12)*BB 
RKO(17)=RKO(17)*BB 
DO 101=1,17 
SLN(I)=2.30258*SL(I) 
ACTF(I)=1.987*SLN(I)/1.8 
RKJ(I)=RKO(I)*EXP(SLN(I)/525.0) 
RKM(I)=RKO(I)*EXP(SLN(I)/565.0) 
RKN(I)=RKO(I)*EXP(SLN(I)/580.0) 
RKH(I)=RKO(I)*EXP(SLN(I)/595.0) 
10 RKL(I)=RKO(I)*EXP(SLN(I)/541.0) 
PRINT11 
11 FORMAT(1H-,63H I RRJ(I) RKL(I) RKM(I) RKN(I)) 
1 RRK(I)) 
DO 131=1,17 
PRINT12,I,RKJ(I),RKL(I),RKM(I),RKN(I),RKH(I) 
12 FORMAT(1H0,13,5E12.4) 
13 CONTINUE 
PRINT40 
40 FORMAT(1H-,63H I RKO(I) SLN(I) ACTE(I) RKH(I)) 
1 RKL(I)) 
DO 50 I=1,17 
PRINT51,I,RKO(I),SLN(I),ACTE(I),RKH(I),RKL(I) 
50 CONTINUE
APPENDIX C

HYDROCARBON PHASE CONCENTRATION PREDICTION MODEL

The values of the frequency factors and activation energies may be used to predict the product distribution and the total conversion for any temperature between 81°F. and 135°F., a 95% H$_2$SO$_4$ catalyst, and any propylene feed concentration between 0.125 and .224 lb./lb. feed.

A derivation of the prediction model and the corresponding computer program, LS, flow diagram and print-out follow this discussion. The inputs to the program are

(1) The volumetric ratio of propylene to isobutane in the feed - R
(2) The volumetric fraction of acid in the reactor - ACID
(3) The volumetric feed rate - CCI
(4) The volumetric product rate - CCO
(5) The reaction temperature - TEMP
(6) The pressure - PRESS
(7) The density of the catalyst - Densa
(8) The proportion between the saturate concentrations and corresponding ionic concentrations - Z

The outputs are:

(1) TEMP
(2) PRESS

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
(3) R

(4) The olefin space velocity - S

(5) ACID

(6) The molar concentration of the catalyst - ACIDC

(7) The mean residence time - TR

(8) The molar feed rate of propylene - PROPM

(9) The molar feed rate of isobutane - BHTM

(10) The total molar product rate - SUMM

(11) The total weight feed rate - TOTW

(12) The product weight fraction - WHC(I)

(13) The product mole fractions - CMFHC(I)

Derivation of Prediction Model

With a value of $X = 1.0$ the equations 2-3.1, 2-3.9, 2-3.11, 2-3.12, 2-3.14 through 2-3.16, and 2-3.18 may be used in conjunction with equations 2-2.3 through 2-2.9 to develop a model to predict concentrations with the knowledge of rate constants.

1. The rate constants may be calculated for a temperature by:

$$k_1 = k_{o_1} e^{-E_1/RT}$$

2. The value for $r_{C_3}$ may be calculated readily from equation 2-3.1.

$$r_{C_3} = k_1 [C_3=][HX]$$
3. The value for \( r_{iC_8} \) may be calculated from equation 2-3.9.

\[
r_{iC_8} = k_9[iC_4^+X^-]
\]

4. The values of the remaining rates may be calculated using equations 2-3.11, 2-3.12, 2-3.14 through 2-3.16 and 2-3.18 with substitution for \( r_{C_i} \) by equation 2-2.3 through 2-2.9 using \( r_{C_6} \) as an example:

\[
r_{C_6} = k_4[C_6^+X^-][iC_4] \quad \text{2-2.5)}
\]

\[
= k_4[C_6][iC_4]Z \quad \text{C-1)}
\]

and

\[
[iC_4^+X^-] = [iC_4][C_3^=]Z/[C_3^=]_b \quad \text{C-2)}
\]

The six resulting equations are:

\[
k_{11}[iC_4]Z \left( \frac{[C_3^=]^2}{[C_3^=]_b} \right) = \left\{ k_5[iC_7] + k_8[C_{10}] + \frac{\left( k_3[iC_5] + k_4[C_6] + k_7[C_9] \right)}{2} \right\}[iC_4]Z \quad \text{C-3)}
\]

\[
k_{12}[iC_7]Z = k_4[C_6][iC_4]Z \quad \text{C-4)}
\]
\[ 2k_{14}[iC_5] = k_3[iC_5][iC_4]Z + k_4[C_6][iC_4]Z - k_7[C_9][iC_4]Z \quad (C-5) \]

\[ 2k_{15}[iC_7][C_3]Z = k_3[iC_5][iC_4]Z - k_4[C_6][iC_4]Z + k_7[C_9][iC_4]Z + 2k_8[C_10][iC_4]Z \quad (C-6) \]

\[ k_{16} \frac{[iC_5][iC_4][C_3]Z}{[C_3]_b} = k_7[C_9][iC_4]Z \quad (C-7) \]

\[ 2k_{16}[C_10]Z = k_3[iC_5][iC_4]Z - k_4[C_6][iC_4]Z + k_7[C_9][iC_4]Z \quad (C-8) \]

From equation (C-4) an expression for \([iC_7]\) is:

\[ [iC_7] = \frac{k_4}{k_{12}} \frac{[C_6][iC_4]}{} \quad (C-4) \]

Likewise, (C-2) yields \([iC_5] \]

\[ [iC_5] = \frac{k_7}{k_{16}} \frac{[iC_4]}{[C_9][C_3]_b} \quad (C-5) \]
If these are substituted into C-3, C-5 and C-6 and the common terms in these equations together with C-8 are cancelled, the following equations result.

\[ k_{11}[C_3 \equiv] = \frac{k_3}{2} [iC_5] + \left( \frac{k_4k_5}{k_{12}} [iC_4] + 0.5 \right)C_6 \]

\[ + \frac{k_7}{2} [C_9] + k_8[C_{10}] \quad \text{C-9} \]

\[ 0 = k_{13}[iC_4]Z[iC_5] + k_4[iC_4]Z[C_6] \]

\[ - \left( \frac{2k_{14}k_7[C_3 \equiv][HX]}{k_{16}[C_3 \equiv]_b} + k_7[iC_4]Z \right)C_9 + 0[C_{10}] \quad \text{C-10} \]

\[ 0 = k_3[iC_5] - \left( \frac{2k_{15}k_4[C_3 \equiv]}{k_{12}} + k_4 \right)C_6 + k_7[C_9] \]

\[ + 2k_8[C_{10}] \quad \text{C-11} \]

\[ 0 = k_3[iC_4][iC_5] - k_4[iC_4][C_6] + k_7[iC_4][C_9] \]

\[ - 2k_{18}[C_{10}] \quad \text{C-12} \]

5. The resulting four equations, C-9 through C-12, may be solved by matrix algebra for the four unknowns \( [iC_5], [C_6], [C_9] \)
and $C_{10}$.

6. The value for $[iC_7]$ may be obtained from $C-4$.

7. The values for $r_{C_i}$ now may be calculated from equations comparable to $C-1$.

$$r_{C_6} = k_4[C_6][iC_4]Z \quad \text{(C-1)}$$

The value for $r_{iC_4}$ is equal to the number of moles of $iC_4$ in each of the products.

<table>
<thead>
<tr>
<th>Product</th>
<th>Moles $iC_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3$</td>
<td>0</td>
</tr>
<tr>
<td>$iC_5$</td>
<td>1</td>
</tr>
<tr>
<td>$C_6$</td>
<td>1</td>
</tr>
<tr>
<td>$iC_7$</td>
<td>1</td>
</tr>
<tr>
<td>$iC_8$</td>
<td>2</td>
</tr>
<tr>
<td>$C_9$</td>
<td>2</td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>1</td>
</tr>
</tbody>
</table>

Thus, $r_{iC_4}$ is equal to

$$r_{iC_4} = r_{iC_5} + r_{C_6} + r_{iC_7} + 2r_{iC_8} + 2r_{C_9} + r_{C_{10}} \quad \text{(C-13)}$$

The product rate of $iC_4$ is then

$$P_{iC_4} = F_{iC_4} - r_{iC_4} \quad \text{(C-14)}$$
6. The weight fraction in the product of each component $i$ is then

\[
W_{HC_i} = \frac{(r_i)M_i}{\sum_{i=1}^{g} (r_i)M_i}
\]

C-15)

where $W_{HC_i}$ is the weight fraction of component $i$, and $M_i$ is the molecular weight of component $i$. 

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
FLOW DIAGRAM
OF COMPUTER PROGRAM LS

Start

I = 0

I = I + 1

Read CMW(I), DENS(I)

No

I = 8

Yes

Read R, ACID, CCI, CCO, TEMP, PRESS, DENS(A), Z

Convert TEMP
TEMP = TEMP + 460

Calculate rate constants from equation 2-15 using values of RKO(I) and SLN(I) from PR;
RK(J) = RKO(J)EXP(SLN(I)/TEMP)

Calculate COLE(2), ACIDC, VFR, VPR, TOTW, PROPM, BUTM, TR, S, CONCA(1) as in Program EX

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Equations to solve are in form of
\[ Y(K) = A(K, 1) \text{CONCA}(3) + A(K, 2) \text{CONCA}(4) \]
\[ + A(K, 3) \text{CONCA}(7) + A(K, 4) \text{CONCA}(8) \]

\[ K = 1 \text{ to } 4 \]

Calculate values of \( Y(K) \) and \( A(K, L) \)

\( (K = 1 \text{ to } 4, \ L = 1 \text{ to } 4) \)

Calculate \( \text{CONCA}(3), \text{CONCA}(4), \text{CONCA}(7) \)

and \( \text{CONCA}(8) \) using Cramer's Rule

Calculate \( \text{CONCA}(5) \) from equation C-4

Calculate \( \text{CONCA}(7) \) from

\[ \text{CONCA}(6) = \frac{\text{RK}(9) \times \text{COLE}(2)}{\text{RK}(6) \times 10^{-9}} \]

Calculate the molar product rate of propane \( \text{CMP}(2) \)

\[ \text{CMP}(2) = \frac{\text{COLE}(2)}{\text{ACIDC} \times \text{RK}(1)} \]

\[ I = 2 \]

\[ I = I + 1 \]
Calculate the molar product rate CMP(I) from

\[ \text{CMP(I)} = \text{RK(I)} \times \text{CONCA(I)} \times Z \times \text{CONCA}(1) \]

Yes

Calculate the molar product rate of iC\textsubscript{4} - CMP(I) Material Balance Equation C-13

Calculate the component mole fractions in the hydrocarbon phase CMFHC(I)

Calculate the weight fractions in the hydrocarbon phase WHC(I)

Print TEMP, PRESS, R, S, ACID, ACIDC, TR, PROPMM, BUTM, TOTW

\[ I = 0 \]

\[ I = I + 1 \]

Print WHC(I), CMFHC(I)
No

I = 8

Yes

Stop
DIMENSION WHC(20),PDC(20),CMT(20),CWP(20),CMFHC(20),CONWA(120),CONCHI(20),CONCA(20),COLE(20),CION(20),RK(20),DENS(20),CMW(20),1Y(20),A(20,20)

DO11 I=1,8
READ0,J,CMW(I),DENS(I)
11 CONTINUE

123 READ17,R,ACID,CC1,CC0,TEMP,PRESS,DENSA,Z
17 FORMAT(6X,8F8.4)
TEMP=TEMP+460.0

RK(1)=0.5818E09*EXP(-0.2132E04/TEMP)
RK(2)=0.1189E14*EXP(0.1131E02/TEMP)
RK(3)=0.1893E13*EXP(0.2683E02/TEMP)
RK(4)=0.2325E13*EXP(0.1110E02/TEMP)
RK(5)=0.2704E13*EXP(0.1058E02/TEMP)
RK(6)=0.3078E13*EXP(0.1145E02/TEMP)
RK(7)=0.3461E13*EXP(0.1097E02/TEMP)
RK(8)=0.3840E13*EXP(0.1068E02/TEMP)
RK(9)=0.1411E09*EXP(-0.3593E03/TEMP)
RK(10)=3.2379E21*EXP(2.30258*(-156.038)/TEMP)
RK(11)=0.1143E20*EXP(-0.2137E04/TEMP)
RK(12)=0.2695E10*EXP(-0.9736E03/TEMP)
RK(13)=0.2095E24*EXP(-0.5193E04/TEMP)
RK(14)=0.9340E13*EXP(-0.3342E04/TEMP)
RK(15)=2.1374E19*EXP(2.30258*(-1019.45)/TEMP)
RK(16)=2.4520E21*EXP(2.30258*(-1041.89)/TEMP)
RK(17)=0.1601E16*EXP(-0.7605E04/TEMP)
Z=Z+1.0E-05

COLE(2)=0.999*(R/(R+1.0))/(.154/1.154)
COLE(2)=COLE(2)*1.0E-05

ACIDC=0.95*DENSA/98.1
VFR=CCI*(0.002118)
VPR=CC0*(0.002118)
TOTW=VFR*(R/(R+1.0)*32.54+35.08/(R+1.0))
\[
\begin{align*}
\text{PROPW} &= \text{VFR} \times \frac{R}{(R+1.0)} \times 32.54 \\
\text{BUTW} &= \text{VFR} \times \left(\frac{35.08}{(R+1.0)}\right) \\
\text{PROPM} &= \text{PROPW} \times (42.1 \times 0.0347) \\
\text{BUTM} &= \text{BUTW} \times (58.1 \times 0.0347) \\
\text{VHCR} &= 0.0579 \times (1.0 - \text{ACID}) \\
\text{TR} &= \text{VHCR} / \text{VFR} \\
S &= \left(\frac{\text{VFR} \times R}{(R+1.0)}\right) / (\text{ACID} \times 0.0579) \\
\text{CONWA}(1) &= 0.0007 \\
\text{CONCA}(1) &= \text{CONWA}(1) \times \text{DENS} / \text{CMW}(1) \\
Y(1) &= \text{RK}(11) \times (\text{COLE}(2) \times 2.0) / 1.0E-09 \\
Y(2) &= 0.0 \\
Y(3) &= 0.0 \\
Y(4) &= 0.0 \\
A(1,1) &= \text{RK}(3) / 2.0 \\
A(1,2) &= \text{RK}(4) \times (\text{RK}(5) / \text{RK}(12)) \times \text{CONCA}(1) + 0.5 \\
A(1,3) &= \text{RK}(7) / 2.0 \\
A(1,4) &= \text{RK}(8) \\
A(2,1) &= \text{RK}(3) \times \text{CONCA}(1) \times Z \\
A(2,2) &= \text{RK}(4) \times \text{CONCA}(1) \times Z \\
A(2,3) &= (2.0 \times \text{RK}(14) \times \text{RK}(7) \times \text{ACID} / \text{RK}(16)) \times (1.0E-09) / \text{COLE}(2)) \times \text{RK}(7) \times \text{CONCA}(1) \times Z \\
A(2,4) &= 0.0 \\
A(3,1) &= \text{RK}(3) \\
A(3,2) &= -\text{RK}(4) \times (2.0 \times \text{RK}(15) / \text{RK}(12)) \times \text{COLE}(2) + 1.0 \\
A(3,3) &= \text{RK}(7) \\
A(3,4) &= 2.0 \times \text{RK}(8) \\
A(4,1) &= \text{RK}(3) \times \text{CONCA}(1) \\
A(4,2) &= -\text{RK}(4) \times \text{CONCA}(1) \\
A(4,3) &= \text{RK}(7) \times \text{CONCA}(1) \\
A(4,4) &= 2.0 \times \text{RK}(17) \\
AC &= -A(2,1) \times A(1,2) \times A(3,3) \times A(4,4) + A(1,3) \times A(3,4) \times A(4,2) + A(1,4) \times A(4,3) \\
1 &= A(3,2) - A(1,4) \times A(4,3) \times A(4,2) - A(1,2) \times A(4,3) \times A(3,4) - A(4,4) \times A(3,2) \times A \\
2 &= A(1,3) + A(2,2) \times A(2,2) \times A(1,1) \times A(3,3) \times A(4,4) + A(1,4) \times A(4,3) \times A(3,1) + A(4,1) \times A \\
3 &= A(4,4) \times A(1,3) - A(1,4) \times A(3,3) \times A(4,1) - A(1,1) \times A(4,3) \times A(3,4) - A(4,4) \times A(3,1) \\
4 &= A(1,3) - A(2,3) \times A(1,1) \times A(3,2) \times A(4,4) + A(1,4) \times A(4,2) \times A(3,1) + A(4,1) \\
\end{align*}
\]
2 57

5*A(3,4)*A(1,2)-A(1,4)*A(3,2)*A(4,1)-A(1,1)*A(4,2)*A(3,4)-A(4,4)*A(1,2)
AZ=-A(3,2)*Y(1)*A(2,3)*A(4,4)*Y(2)*A(1,4)*A(4,3)*Y(4)*A(2,4)*A(1,1)
13-Y(4)*A(1,4)*A(2,3)-Y(1)*A(4,3)*A(2,4)-Y(2)*A(4,4)*A(1,3)*A(3,3)
2)*Y(1)*A(2,2)*A(4,4)*A(1,4)*A(4,2)*Y(4)*A(4,1)*A(2,4)-A(1,2)-Y(4)*A
3(1,4)*A(2,2)-Y(1)*A(4,4)*A(1,2)-A(3,4)^*Y(1)*A
4(2,2)*A(4,3)*Y(2)*A(1,3)*A(4,2)*Y(4)*A(2,3)*A(1,2)-Y(4)*A(1,3)*A(2,1)
5,21-Y(1)*A(4,2)*A(2,3)-Y(2)*A(4,3)*A(1,2)
AM=+A(3,1)*Y(1)*A(2,3)*A(4,4)*Y(2)*A(1,4)*A(4,3)*Y(4)*A(2,4)*A(1,1)
13)-Y(4)*A(2,3)*A(1,4)-Y(1)*A(4,3)*A(2,4)-Y(2)*A(4,4)*A(1,3)*A(3,3)
2)*Y(2)*A(1,1)*A(4,4)*A(1,4)*A(2,1)*Y(1)*A(4,1)*A(2,4)*Y(2)*A
3(1,4)*A(4,1)-Y(4)*A(1,1)*A(2,4)-Y(1)*A(4,4)*A(2,1)-A(3,4)*Y(2)*A
4(1,1)*A(4,3)*Y(4)*A(1,3)*A(2,1)+Y(1)*A(4,1)*A(2,3)+Y(2)*A(1,3)*A(2,1)
5,1)-Y(4)*A(1,1)*A(2,3)-Y(1)*A(4,3)*A(2,1)
AX=+A(3,1)*Y(2)*A(1,2)*A(4,4)*Y(4)*A(1,4)*A(2,2)+Y(1)*A(4,2)*A(1,2)
14)-Y(2)*A(1,4)*A(4,2)*Y(4)*A(1,2)*A(2,4)-Y(1)*A(4,4)*A(2,2)-A(3,2)
2)*Y(2)*A(1,4)*A(4,4)*A(1,4)*A(2,1)+Y(1)*A(4,1)*A(2,4)*Y(2)*A
3(1,4)*A(4,1)-Y(4)*A(1,1)*A(2,4)-Y(1)*A(4,4)*A(2,1)-A(3,4)*Y(4)*A
4(1,1)*A(2,2)+Y(1)*A(4,2)*A(2,1)+Y(2)*A(4,1)*A(1,2)-Y(1)*A(2,2)*A(4)
5,1)-Y(2)*A(1,1)*A(4,2)-Y(4)*A(2,1)*A(1,2)
AY=+A(3,1)*Y(4)*A(1,2)*A(2,3)+Y(1)*A(4,3)*A(2,2)+Y(2)*A(4,2)*A(1,1)
13)-Y(1)*A(2,3)*A(4,2)-Y(2)*A(4,3)*A(1,2)-Y(4)*A(2,2)*A(1,3)-A(3,2)
2)*Y(4)*A(2,3)*A(1,1)+Y(1)*A(4,3)*A(2,1)+Y(2)*A(4,4)*A(1,3)-Y(1)*A
3(2,3)*A(4,1)-Y(2)*A(1,1)*A(4,3)*Y(4)*A(2,1)*A(1,3)+A(3,3)*Y(4)*A
4(1,1)*A(2,2)+Y(1)*A(4,2)*A(2,1)+Y(2)*A(4,1)*A(1,2)-Y(1)*A(2,2)*A(4)
5,1)-Y(2)*A(1,1)*A(4,2)-Y(4)*A(2,1)*A(1,2)
CONCA(3)=AZ/AC
CONCA(4)=AW/AC
CONCA(7)=AX/AC
CONCA(8)=AY/AC
CMP(2)=COLE(2)*ACIDC*RK(1)
CONCA(6)=RK(9)/RK(6)+COLE(2)/(1.OE-09)
CONCA(5)=RK(4)/RK(12)*CONCA(4)*CONCA(1)
CMPT=0.0
DOL1LI=3,8
CMP(I) = RK(I) * CONCA(I) * Z * CONCA(1)

CMP = CMP + CMP(I)

CMP(I) = BUTM - CMP - CMP(6) - CMP(7)

CON = 0.0

DO 2211 I = 1, 8

CMFHC(I) = CMP(I) / (CMP + CMP(1) + CMP(2))

CONCH(I) = CMFHC(I) * CMW(I)

CON = CON + CONCH(I)

DO 333 I = 1, 8

WHC(I) = CONCH(I) / CON

PRINT 187, AC, AZ, AW, AX, AY

107 FORMAT(1HO, 5E14.7)

PRINT 25

25 FORMAT(1H-, 5I1 TEMP, PRESS, R, S, ACID, ACIDC, )

PRINT 30, TEMP, PRESS, R, S, ACID, ACIDC

30 FORMAT(1HO, 2F8.2, F8.5, F10.7, 2F8.5)

PRINT 35

35 FORMAT(1H-, 3I1 TR, PROPM, BUTM, TOTW, )

PRINT 40, TR, PROPM, BUTM, TOTW

40 FORMAT(1HO, F7.4, 3F8.5)

PRINT 45

45 FORMAT(1H-, 3I1 I, WHC(I), CMFHC(I), )

DO 511 I = 1, 8

PRINT 50, I, WHC(I), CMFHC(I)

50 CONTINUE

GOTO 123

51 CONTINUE

GOTO 123

4000 STOP

END
VITA

John Randolph Langley was born on March 25, 1942, at Fort Jackson, South Carolina. In 1946 his parents, Mr. and Mrs. John E. Langley, and he moved to Baton Rouge, Louisiana, where he currently resides.

Mr. Langley began his college education in September 1960 at Auburn University, Auburn, Alabama. He transferred to Louisiana State University, Baton Rouge, in September 1962. In January of 1965 he received the Bachelor of Science degree in Chemical Engineering.

He entered the Graduate School of Louisiana State University in February 1965 and received the Master of Science degree in Chemical Engineering in January of 1967. He then continued work toward the Doctor of Philosophy degree. While in Graduate School he has held a National Aeronautics and Space Administration Research Assistantship, the Esso Research Laboratories Assistantship, the Jefferson Chemical Company Fellowship, and a National Science Foundation Assistantship. While in Graduate School Mr. Langley became a member of Phi Lambda Upsilon and an associate member of the Society of Sigma Xi.

On December 21, 1963, Mr. Langley married the former Sandra Courtney Langhart, of Baton Rouge. They have one child, a daughter, Juliann.
EXAMINATION AND THESIS REPORT

Candidate: John Randolph Langley
Major Field: Chemical Engineering
Title of Thesis: The Kinetics of Alkylation of Isobutane with Propylene Using a Sulfuric Acid Catalyst

Date of Examination: April 28, 1969

Approved:

[Signatures]
Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.