Ultraviolet Spectroscopic and Nuclear Magnetic Resonance Studies of the Enol-Keto Tautomerism in Beta-Diketones.

Jang Kuo
Louisiana State University and Agricultural & Mechanical College

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UV SPECTROSCOPIC AND NUCLEAR MAGNETIC RESONANCE STUDIES OF THE ENOL-KETO TAUTOMERISM IN \( \beta \)-DIKETONES

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 Chemistry

by

Jang Kuo
B.S., National Taiwan University, 1958
M.S., Louisiana State University, 1963
August, 1966
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The author wishes to express his appreciation to Dr. R. V. Nauman, under whose direction this work was carried out.

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The author expresses his appreciation to the Dr. Charles E. Coates Memorial Fund for the financial assistance pertinent to the publication of this doctoral dissertation.
TABLE OF CONTENTS

| ACKNOWLEDGMENTS | .................................................. | ii |
| LIST OF TABLES | .................................................. | iv |
| LIST OF FIGURES | .................................................. | v |
| ABSTRACT | .................................................. | x |

CHAPTER

1. UV SPECTROSCOPIC STUDIES OF THE ENOL–KETO TAUTOMERISM IN \( \beta \)-DIKETONES | .................................................. | 1 |
   I. INTRODUCTION | .................................................. | 1 |
   II. EXPERIMENTAL | .................................................. | 16 |
      A. Compounds | .................................................. | 16 |
      B. Spectral Measurements | .................................................. | 17 |
   III. RESULTS AND DISCUSSION | .................................................. | 22 |
   IV. SUMMARY | .................................................. | 84 |

2. NUCLEAR MAGNETIC RESONANCE STUDIES OF THE ENOL–KETO TAUTOMERISM IN \( \beta \)-DIKETONES | .................................................. | 87 |
   I. INTRODUCTION | .................................................. | 87 |
   II. EXPERIMENTAL | .................................................. | 94 |
   III. RESULTS AND DISCUSSION | .................................................. | 96 |
   IV. SUMMARY | .................................................. | 113 |

SELECTED BIBLIOGRAPHY | .................................................. | 114 |
VITA | .................................................. | 118 |
LIST OF TABLES

CHAPTER 1. UV SPECTROSCOPIC STUDIES OF THE ENOL-KETO
TAUTOMERISM IN 3-DIKETONES

TABLE

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Absorption Spectra in Cyclohexane at Room Temperature</td>
<td>25</td>
</tr>
<tr>
<td>2. Absorption Spectra in Isopropylalcohol at Room Temperature</td>
<td>26</td>
</tr>
<tr>
<td>3. Intramolecular Charge Transfer Bands</td>
<td>30</td>
</tr>
<tr>
<td>4. Energy Levels of 3-Diketones</td>
<td>82</td>
</tr>
</tbody>
</table>

CHAPTER 2. NUCLEAR MAGNETIC RESONANCE STUDIES OF THE
ENOL-KETO TAUTOMERISM IN 3-DIKETONES

TABLE

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Proton Chemical Shifts in Pure 3-Diketones</td>
<td>97</td>
</tr>
<tr>
<td>2. Percentage of Enol Tautomers, Equilibrium Constants, $\Delta G^0$, $\Delta S^0$ of the Keto-Enol Tautomerism</td>
<td>105</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

**CHAPTER 1. UV SPECTROSCOPIC STUDIES OF THE ENOL-KETO TAUTOMERISM IN 1,3-DIKETONES**

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Term-level Diagram</td>
<td>7</td>
</tr>
<tr>
<td>2. A. Apparatus Arrangement for Phosphorescence Measurement</td>
<td>21</td>
</tr>
<tr>
<td>B. Apparatus Arrangement for Total Emission Measurement</td>
<td>21</td>
</tr>
<tr>
<td>3. Absorption Spectra in Cyclohexane at Room Temperature</td>
<td>23</td>
</tr>
<tr>
<td>a. Benzoylacetone</td>
<td></td>
</tr>
<tr>
<td>b. Benzoyltrifluoroacetone</td>
<td></td>
</tr>
<tr>
<td>c. Dibenzoylmethane</td>
<td></td>
</tr>
<tr>
<td>d. 2-Bromo-1,3-diphenyl-1,3-propanedione</td>
<td></td>
</tr>
<tr>
<td>e. Dibenzalacetone</td>
<td></td>
</tr>
<tr>
<td>4. Absorption Spectra in Isopropylalcohol at Room Temperature</td>
<td>24</td>
</tr>
<tr>
<td>a. Benzoylacetone</td>
<td></td>
</tr>
<tr>
<td>b. Benzoyltrifluoroacetone</td>
<td></td>
</tr>
<tr>
<td>c. Dibenzoylmethane</td>
<td></td>
</tr>
<tr>
<td>d. 2-Bromo-1,3-diphenyl-1,3-propanedione</td>
<td></td>
</tr>
<tr>
<td>e. Dibenzalacetone</td>
<td></td>
</tr>
<tr>
<td>5. Absorbance vs. Concentration of Dibenzoylmethane in Isopropylalcohol</td>
<td>33</td>
</tr>
<tr>
<td>a. 340 nm peak</td>
<td></td>
</tr>
<tr>
<td>b. 250 nm peak</td>
<td></td>
</tr>
<tr>
<td>c. 225 nm peak</td>
<td></td>
</tr>
<tr>
<td>6. Absorption Spectra of Dibenzoylmethane in Isopropylalcohol at Room Temperature</td>
<td>34</td>
</tr>
<tr>
<td>a. Before Addition of HCl</td>
<td></td>
</tr>
<tr>
<td>b. After Addition of HCl for 3 minutes</td>
<td></td>
</tr>
<tr>
<td>c. After Addition of HCl for 5 minutes</td>
<td></td>
</tr>
<tr>
<td>FIGURE</td>
<td>Absorption Spectra of Dibenzoylmethane in IPMP</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>7.</td>
<td>a. at 25°C</td>
</tr>
<tr>
<td></td>
<td>b. at 77K</td>
</tr>
<tr>
<td></td>
<td>c. at 77K after Irradiation with the A-H6</td>
</tr>
<tr>
<td></td>
<td>d. at 25°C after Irradiation at 77K</td>
</tr>
<tr>
<td>8.</td>
<td>a. at 25°C</td>
</tr>
<tr>
<td></td>
<td>b. at 77K</td>
</tr>
<tr>
<td></td>
<td>c. at 77K after Irradiation with the A-H6</td>
</tr>
<tr>
<td></td>
<td>d. at 25°C after Irradiation at 77K</td>
</tr>
<tr>
<td>9.</td>
<td>a. at 25°C</td>
</tr>
<tr>
<td></td>
<td>b. at 77K</td>
</tr>
<tr>
<td></td>
<td>c. at 77K after Irradiation with the A-H6</td>
</tr>
<tr>
<td></td>
<td>d. at 25°C after Irradiation at 77K</td>
</tr>
<tr>
<td>10.</td>
<td>a. at 25°C</td>
</tr>
<tr>
<td></td>
<td>b. at 77K</td>
</tr>
<tr>
<td></td>
<td>c. at 77K after Irradiation with the A-H6</td>
</tr>
<tr>
<td></td>
<td>d. at 25°C after Irradiation at 77K</td>
</tr>
<tr>
<td>11.</td>
<td>a. at 25°C</td>
</tr>
<tr>
<td></td>
<td>b. at 77K</td>
</tr>
<tr>
<td></td>
<td>c. at 77K after Irradiation with the A-H6</td>
</tr>
<tr>
<td></td>
<td>d. at 25°C after Irradiation at 77K</td>
</tr>
<tr>
<td>12.</td>
<td>a. at 25°C</td>
</tr>
<tr>
<td></td>
<td>b. at 77K</td>
</tr>
<tr>
<td></td>
<td>c. at 77K after Irradiation with the A-H6</td>
</tr>
<tr>
<td>FIGURE</td>
<td>Absorption Spectra in IPMP at Room Temperature.</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>13.</td>
<td>a. 2-Bromo-1,3-diphenyl-1,3-propanedione</td>
</tr>
<tr>
<td></td>
<td>b. 2-Bromo-1,3-diphenyl-1,3-propanedione after</td>
</tr>
<tr>
<td></td>
<td>Irradiation at Room Temperature</td>
</tr>
<tr>
<td></td>
<td>c. Dibenzoylmethane</td>
</tr>
<tr>
<td></td>
<td>a. Dibenzoylmethane</td>
</tr>
<tr>
<td></td>
<td>b. Irradiated 2-Bromo-1,3-diphenyl-1,3-propanedione</td>
</tr>
<tr>
<td></td>
<td>c. Irradiated Dibenzoylmethane</td>
</tr>
<tr>
<td>15.</td>
<td>Absorption Spectra of Dibenzoylmethane in IPMP at 77°K</td>
</tr>
<tr>
<td></td>
<td>a. before Irradiation</td>
</tr>
<tr>
<td></td>
<td>b. after Irradiation with the A-H6 for 15 minutes</td>
</tr>
<tr>
<td></td>
<td>c. after Irradiation with the A-H6 for 25 minutes</td>
</tr>
<tr>
<td></td>
<td>d. after Irradiation with the A-H6 for 35 minutes</td>
</tr>
<tr>
<td></td>
<td>e. after Irradiation with the A-H6 for 60 minutes</td>
</tr>
<tr>
<td>16.</td>
<td>Absorption Spectra of Acetylacetone in IPMP</td>
</tr>
<tr>
<td></td>
<td>a. at 25°C</td>
</tr>
<tr>
<td></td>
<td>b. at 77°K before Irradiation</td>
</tr>
<tr>
<td></td>
<td>c. at 77°K after Irradiation with the A-H6 for 10 minutes</td>
</tr>
<tr>
<td></td>
<td>d. at 77°K after Irradiation with the A-H6 for 30 minutes</td>
</tr>
<tr>
<td>17.</td>
<td>Blue Phosphorescence Spectra in EPA</td>
</tr>
<tr>
<td></td>
<td>a. Dibenzoylmethane</td>
</tr>
<tr>
<td></td>
<td>b. Benzoylacetone</td>
</tr>
<tr>
<td></td>
<td>c. Benzoyltrifluoroacetone</td>
</tr>
<tr>
<td></td>
<td>d. 2-Bromo-1,3-diphenyl-1,3-propanedione</td>
</tr>
<tr>
<td></td>
<td>e. Benzaldehyde</td>
</tr>
<tr>
<td>18.</td>
<td>Green Phosphorescence Spectra in EPA Exciting at the Intramolecular Charge Transfer Band</td>
</tr>
<tr>
<td></td>
<td>a. Dibenzoylmethane</td>
</tr>
<tr>
<td></td>
<td>b. Benzoylacetone</td>
</tr>
<tr>
<td></td>
<td>c. Benzoyltrifluoroacetone</td>
</tr>
</tbody>
</table>

vii
### LIST OF FIGURES (continued)

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>19. Phosphorescence Spectra of Irradiated Dibenzoylmethane</td>
<td>62</td>
</tr>
<tr>
<td>a. Blue and Green Phosphorescences in 3-Methylpentane</td>
<td></td>
</tr>
<tr>
<td>b. Blue Phosphorescence in EPA</td>
<td></td>
</tr>
<tr>
<td>c. Green Phosphorescence in EPA</td>
<td></td>
</tr>
<tr>
<td>20. Phosphorescence Spectra of Benzoylacetone in 3-Methylpentane</td>
<td>64</td>
</tr>
<tr>
<td>a. Before Irradiation</td>
<td></td>
</tr>
<tr>
<td>b. After Irradiation with the A-He for 10 minutes at 77°K</td>
<td></td>
</tr>
<tr>
<td>21. Phosphorescence Spectra of Benzoyltrifluoroacetone in 3-Methylpentane</td>
<td>65</td>
</tr>
<tr>
<td>a. Initially</td>
<td></td>
</tr>
<tr>
<td>b. After 10 minutes of Irradiation with the Exciting light</td>
<td></td>
</tr>
<tr>
<td>c. After 25 minutes of Irradiation with the Exciting light</td>
<td></td>
</tr>
<tr>
<td>22. Excitation Spectra of Blue Phosphorescence in EPA</td>
<td>67</td>
</tr>
<tr>
<td>a. Benzoylacetone</td>
<td></td>
</tr>
<tr>
<td>b. Benzoyltrifluoroacetone</td>
<td></td>
</tr>
<tr>
<td>c. Dibenzoylmethane</td>
<td></td>
</tr>
<tr>
<td>d. Benzaldehyde</td>
<td></td>
</tr>
<tr>
<td>23. Excitation Spectra of the Green Phosphorescence in EPA</td>
<td>68</td>
</tr>
<tr>
<td>a. Dibenzoylmethane</td>
<td></td>
</tr>
<tr>
<td>b. Benzoylacetone</td>
<td></td>
</tr>
<tr>
<td>c. Benzoyltrifluoroacetone</td>
<td></td>
</tr>
<tr>
<td>24. A. Absorption Spectrum of Dibenzoylmethane in EPA at 77°K</td>
<td>69</td>
</tr>
<tr>
<td>B. Green Phosphorescence Excitation Spectrum of Dibenzoylmethane in EPA at 77°K</td>
<td>69</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (continued)

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.</td>
<td>Fluorescence and Absorption Spectra of Dibenzoylmethane at 77°K</td>
<td>73</td>
</tr>
<tr>
<td>a.</td>
<td>Absorption Spectrum in IPMP</td>
<td></td>
</tr>
<tr>
<td>b.</td>
<td>Fluorescence Spectrum in IPMP</td>
<td></td>
</tr>
<tr>
<td>c.</td>
<td>Absorption Spectrum in EPA</td>
<td></td>
</tr>
<tr>
<td>d.</td>
<td>Fluorescence Spectrum in EPA</td>
<td></td>
</tr>
</tbody>
</table>

CHAPTER 2. NUCLEAR MAGNETIC RESONANCE STUDIES OF KETO-ENOL TAUTOMERISM IN P-DIKETONES

1. Chemical Shifts of OH Signal vs. Temperature                           | 102  |
2. Temperature vs. Enol Contents                                          | 106  |
3. Temperature Dependence of the Equilibrium Constants                    | 108  |
Keto-enol tautomeric equilibria in β-diketones, which include benzoylacetone, benzoyltrifluoroacetone, dibenzoylmethane; acetylacetone and hexafluoroacetylacetone, have been studied by electronic spectroscopy and nuclear magnetic resonance spectroscopy.

Ultraviolet absorption spectra of β-diketones in cyclohexane and isopropyl alcohol have been recorded at room temperature. Benzoylacetone, benzoyltrifluoroacetone and dibenzoylmethane give three main absorption bands. The longest wavelength band (usually above 285 μ) is assigned as an intramolecular charge transfer band which is the characteristic band of the enol form of β-diketones. The keto form of β-diketones does not have this kind of electronic transition. These intramolecular charge transfer bands have been studied further at 77°K. The intermediate wavelength band appears in the region of 240 μ and 270 μ and the shortest wavelength band appears below 240 μ. All three transitions are $n \rightarrow \pi^*$ transitions.

The photochemical reactions of β-diketones have been observed at 77°K. No photochemical reactions have been detected at room temperature except in the case of 2-bromo-1,3-diphenyl-1,3-propanediione. This photochemical reaction is believed to proceed through a keto-enol equilibrium with an unchelated enol form as the intermediate. β-Diketones exist mainly in the chelated enol form in the hydrocarbon solvent, particularly at 77°K. The less stable forms, the keto form and the
unchelated enol form, can be generated by irradiation of the chelated
enol with U.V. light. Some keto forms exist in the polar solvents.
The keto-enol tautomeric equilibrium has been considered to be an
acid-base equilibrium.

All chelated enols, which have the (n, n*) states as the lowest
excited singlet and triplet states, give green phosphorescences. No
fluorescence has been observed from the chelated enols except in the
case of dibenzoylmethane. It is suggested that in the chelated enol
of dibenzoylmethane the T(2)(n, n*) state is of higher energy than the
S(1)(n, n*) state. Neither phosphorescence nor fluorescence has been
observed from the unchelated enol form of the 3-diketones. The keto
form of the 3-diketones gives a strong blue phosphorescence and no
fluorescence. The life time of these blue phosphorescences is of the
order of 10^{-2} seconds. The vibrational structure of these blue phos­
phorescences and their excitation spectra are similar to that of
benzaldehyde.

A detailed mechanism of the photochemical processes of 3-dike­
tones in the rigid glass has been proposed. This mechanism can be
used to interpret the observed phenomena qualitatively. Methods for
further justification of this mechanism have been suggested.

Nuclear magnetic resonance spectra of 3-diketones have been re­
corded at different temperatures. The effect of temperature on the
keto-enol tautomeric equilibrium in pure 3-diketones has been studied.
The increase in temperature displaces the equilibrium to the keto side.
From the melting point of the compound to the maximum temperature limit of the instrument, 190°C, the major component in the equilibrated system is the chelated enol form. Equilibrium constants for the keto-enol tautomeric equilibrium have been determined at different temperatures. The changes of the standard enthalpies of the keto-enol equilibria have been calculated to be -2.3 Kcal/mole, -3.7 Kcal/mole, -3.6 Kcal/mole and -4.0 Kcal/mole for acetylacetone, hexafluoroacetylacetone, benzoylacetone and dibenzoylmethane, respectively. Other thermodynamic quantities have been obtained at different temperatures. These values are interpreted in terms of the molecular structures.
CHAPTER 1

UV SPECTROSCOPIC STUDIES OF THE ENOL-KETO TAUTOMERISM IN \( \beta \)-DIKETONES

I. Introduction

This study is a continuation of the author's previous work.\(^1\) In the previous study it was shown that dibenzoylmethane exists exclusively in an enol form which is chelated by an intramolecular hydrogen bond. Effects of the intramolecular hydrogen bond on both the absorption spectra and the emission spectra of dibenzoylmethane have been studied. The electronic transition which occurs in the 280 nm region of the spectrum at room temperature has been assigned to be the chromophore band of the cinnamoyl group in the compound. Transitions characteristic of the benzoyl group and the styrene group have been found around the regions of 260 nm and 220 nm, respectively. All of these transitions have been shown to be \( \pi \rightarrow \pi^* \) transitions. Solvent studies have shown that the solvent does not affect the electronic transitions substantially. The absorption bands of the \( \pi \rightarrow \pi^* \)

transitions in the chelated dibenzoylmethane were red-shifted in comparison with the similar bands in \( \beta \)-methoxybenzalacetophenone which could not form an intramolecular hydrogen bond. The electronic transition of the cinnamoyl chromophore at liquid nitrogen temperature (77°K) was red-shifted in comparison with the same transition at room temperature. This has been explained by an increase in the dispersion forces that accompany the increase in solvent density that occurs when the temperature decreases. Upon irradiation with the full intensity of an A-H\( \text{H}_6 \) mercury arc this \( \pi \rightarrow \pi^* \) band of the spectrum at 77°K is blue-shifted, while the same band at room temperature is not affected by irradiation. These results have been explained by suggesting that the intramolecular hydrogen bond breaks upon irradiation at 77°K and is prevented from recombination by the solvent rigidity, while at room temperature any photochemical breaking of the intramolecular hydrogen bond results in recombination and the energy is liberated and is lost through thermal collisions with solvent molecules.

It has been found that dibenzoylmethane in hydrocarbon glass gives two different phosphorescences, one blue and one green. The intensity of the blue phosphorescence builds up with time of excitation, while the intensity of the green phosphorescence decreases slightly as the time of excitation increases. In EPA glass the blue phosphorescence appears as soon as the exciting light strikes the sample, and the green phosphorescence is too weak to be detected. The blue phosphorescence has been suggested to result from a transition primarily localized
in the benzoyl group, and the green phosphorescence is believed to come from a transition characteristic of the cinnamoyl group. Dibenzoylmethane exists entirely in the chelated form in hydrocarbon glass at 77°K. This form does not emit the blue phosphorescence, but absorption of light can convert it to the unchelated form which is capable of emission. The formation of the chelated form does not affect the appearance of the green phosphorescence.

In order to understand the mechanism of the photochemical reactions in dibenzoylmethane at liquid nitrogen temperature and to identify the species which correspond to the blue and the green phosphorescence this study was undertaken. In addition to dibenzoylmethane several other β-diketones including aromatic and aliphatic β-diketones have been investigated.

One of the key problems in photochemistry is the identification of high-energy intermediates formed during reactions. The use of rigid or glassy solvents affords a good method for stabilizing labile products. The usefulness of rigid solvent techniques in studying the photochemistry and spectroscopy of complex molecules has been most clearly brought out in the beautiful work of G.N. Lewis and his school.

2-5

2Lewis, G. N. and D. Lipkin, J. Am. Chem. Soc. 64 2801 (1942).
in which a variety of photo-processes were established and studied by this means. The photoprocesses were photo-oxidation by the loss of an electron, photodissociation into two uncharged radicals, photoioniza-
tion into a positive ion and a negative ion, triplet-state excitation, etc. Photo-enolization and photochemical cis-trans isomerism reactions have been observed.

Upon illumination in rigid media at 77°K, the activated molecule from many organic materials loses an electron and becomes a free radical or a positive ion. The free electron becomes attached to a solvent molecule, to a group of molecules or even to some unique point in the solvent that is determined by its rigid structure. The electron lies in a potential hole which is deep enough so that the large electrostatic field of the ion is unable to dislodge it. This photo-
oxidation reaction has been studied further by Linschitz, et al. They have postulated that the recombination of radicals and electrons formed initially by photo-oxidation of the original molecule will re-
sult in the formation of triplet state. The recombination is viscosity dependent, and at liquid nitrogen temperature may be very slow.

Voorst and Hoijtink\(^9\) have observed the photoejection of electrons from negative hydrocarbon ions in a glassy solution of 2-methyl-tetrahydrofuran at 77°K. McClain and Albrecht\(^10\) have studies N, N, N', N'-tetramethylparaphenylene diamine in 3-methylpentane solution. The solution was frozen to a rigid state in liquid nitrogen and irradiated with ultraviolet light in the absorption band of the amine. The amine undergoes a one-electron ionization to give its colored radical cation and an electron trapped in the solvent matrix. Subsequent infrared illumination caused a burst of blue-green luminescence called stimulated emission which was a recombination luminescence composed of the fluorescence and phosphorescence bands of the amine. They have shown that the system possesses electron traps of several different depths, ranging from shallow, thermally ionizable levels to depths of more than 3 eV.

Symons and Townsend\(^11\) have found that the ultraviolet irradiation of a variety of photochemically active compounds, dissolved in rigid (77°K) glasses that contain ethanol as a major component, produced an intense violet coloration which is lost as soon as the glass softens. They postulated that this violet compound is a free radical


formed from the ethanol by hydrogen atom abstraction. Radical and ra-
dical anions have been found in the flash photolysis of benzaldehyde,
acetophenone and benzil in alcoholic solutions.\textsuperscript{12} Photoenolization
has been studied by Yang and his coworkers.\textsuperscript{13} O-Methylbenzophenone
and O-benzal-benzophenone undergo intramolecular hydrogen transfer to
give their corresponding enols under the influence of ultraviolet
light at room temperature. They postulated that this photoenolization
involved an \( (n, \pi^*) \) triplet state as an intermediate. An \( (n, \pi^*) \)
triplet intermediate was postulated for the photolysis of appropriate
1,2 diketones to 2-hydroxy-cyclobutanones.\textsuperscript{14} Photoisomerization of
stilbene has been investigated. A simple model of cis-trans photo-
isomerization was developed by postulating two forms of different
energies in the intermediate state involved during isomerization.\textsuperscript{15}

Figure 1 is a modern elaboration of Jablonski's diagram,\textsuperscript{16} re-
representing the energies of the various low-lying state of an organic
molecule with respect to the ground state \( S_0 \). The two sets of vibro-
nic states superimposed on \( S_0, S_1, S_2, \ldots \) and \( T_1, T_2, \ldots \) con-
stitute the singlet and triplet manifolds, respectively; transitions

\textsuperscript{13} Yang, N. C. and C. Rivas, op. cit.
\textsuperscript{15} Hammond, G. S., et al., op. cit.
Figure 1. Term-level Diagram
of the system between states of different manifolds are known as intercombinations. The various electronic transitions are classified as radiative or radiationless, represented in Figure 1 by solid and broken lines, respectively. The radiationless transition is generally known as internal conversion when it occurs between states of the same manifold, whereas the radiationless $S_1 \rightarrow T_1$ intercombination is called intersystem crossing. Internal conversion from the lowest emitting levels ($S_1$ or $T_1$) to the ground state, particularly when brought about by the action of another molecule, is often known as quenching. Radiative transition between two states of identical multiplicity is known as fluorescence. Emission from the lowest triplet state to the ground state ($T_1 \rightarrow S_0$) is called phosphorescence.

The currently accepted description of the radiationless process in the rigid or glassy state at low temperature follows.\textsuperscript{17-18} A molecule in an excited vibronic state loses vibrational energy, thereby dropping to the zeroth vibrational level of the excited electronic state. From this state there is a transition, by tunneling between the potential-energy surfaces of the excited and ground electronic states, to a vibrationally excited state of the ground electronic state. Finally, the excess vibrational energy of the ground

\textsuperscript{17}Robinson, G. W. and R. P. Frosch, J. Chem. Phys. 37 1962 (1962).

electronic state is removed by the surrounding medium. It is usually assumed that the loss of vibrational energy is very rapid, so that the rate of radiationless transition is determined by the tunneling step. Except under unusual circumstances, involving strong solute-solvent interaction, it is a consequence of this last assumption that the rate of radiationless transition will be independent of the nature of the surrounding (dense) medium. Recently, Rice, et al.19 have postulated that the rate of transfer of vibrational energy is not rapid relative to the rate of intersystem crossing.

Two rules concerning radiative emission have been formulated which summarize a vast number of observations: (1) the emitting level of a given multiplicity is the lowest excited level of the multiplicity; (2) the character of the emission spectrum of a substance does not depend on the exciting wavelength.20 The essential reason why luminescence from electronic levels other than the lowest excited states is not observed under normal conditions is concerned with the greater efficiency of the competing process of internal conversion between the states of a given multiplicity. Hochstrasser21 has given the following further interpretations: (1) As the exciting radiation


must necessarily be in the high-energy bands, the probability of unimolecular photochemical reactions is greater than if the lower energy levels were initially populated. Such dismutations necessarily give rise to species which have less extended conjugation and which will therefore absorb and emit at higher energies than does the parent molecule. These emissions may obscure the $S_n \rightarrow S_0$ emission; (ii) the initial sample purity must be very high. If, for example, there are present $10^{-2}$ mole percent of impurity with a unit quantum yield of luminescence, then the emission from this impurity may be as strong as the $S_n \rightarrow S_0$ emission. (iii) At normal temperatures the $S_n \rightarrow S_0$ emission will necessarily be quite strongly reabsorbed into the lower singlet electronic states. From the second rule one can deduce that the excitation spectrum, which is obtained by monitoring emission as a function of exciting wave length, should be identical with the absorption spectrum. This has been demonstrated for many compounds and implies that relaxation rates from higher states are much faster than competing intersystem crossing or predissociation. Exceptions have been found in several cases. If the excited molecule is free to isomerize, it was found that the quantum yield of fluorescence was considerably lower when the higher electronic states of the molecule were excited. Other exceptions are found with certain substances at very low pressure in the vapor phase. Under these conditions the

molecule may photodissociate before the excess of vibrational energy is removed by collision. Another possible exception is that of intramolecular energy transfer processes which may occur within very short times ($10^{-12}$ second). Should such a process as intersystem crossing, for example, occur at this rate it would probably compete favorably with the internal conversion process between electronic states.

If intersystem crossing between higher states occurs, it should cause a variation in the ratio of the phosphorescence and the fluorescence quantum yields with exciting wave length. Such a variation has been interpreted to be due to an efficient intersystem crossing between a higher singlet state and a close-lying triplet.\textsuperscript{23}

Interest in the triplet states of molecules has grown considerably since Lewis and Kasha\textsuperscript{24} identified the phosphorescent metastable state as a triplet state. The lowest triplet state of a molecule has particular importance because of three distinguishing features:\textsuperscript{25} (1) It is usually the lowest excited state of the molecule. (2) It has a very long lifetime in comparison with other excited states. (3) It is a distinct chemical species, which is often very reactive. Lewis and Kasha discussed several features which distinguish


\textsuperscript{24}Lewis, G. N. and M. Kasha, J. Am. Chem. Soc. 66 2100 (1944).

\textsuperscript{25}Porter, G. and M. R. Wright, Discussions Faraday Soc. 27 18 (1959).
this triplet emission from fluorescence: e.g. the phosphorescence bands (as observed in a low temperature glass) are narrower and generally show different vibrational structure; and within a given class of molecules, the phosphorescence lifetime is shorter the longer the wavelength of the emission. Phosphorescence is not to be expected from saturated molecules because of the disruptive effect which the production of two electrons with parallel spins would have upon the bonding structure in this type of molecule. Consequently, phosphorescence is more or less confined to molecules with double bonds, which can more easily accommodate the unpaired electrons. Also, this emission is greatly enhanced when the lowest singlet is the \((n, \pi^*)\) type. For most molecules phosphorescence may be observed only in a rigid glass environment at low temperature, but some substances also phosphoresce in the liquid or gas phases. One reason that so few substances phosphoresce in liquid solution is that the long lifetime of the triplet makes it highly susceptible to quenching before it radiates. In molecules such as the aromatic hydrocarbons, radiationless crossing from the upper singlet state \(S_1\) to the triplet \(T_1\) occurs with a rate which is typically of the order of \(10^8\) sec\(^{-1}\) in rigid medium, while the apparently similar conversion from \(T_1\) to the ground state \(S_0\) is not observed in rigid media and must have a rate less than \(10^{-1}\) sec\(^{-1}\) in benzene and other molecules with similar radiative triplet lifetime. If the rates of the two radiationless conversions were of comparable magnitude, no phosphorescence would be observed, and this
is the reason for the absence of phosphorescence in ordinary solutions and gases.

It is well known that whereas the aromatic hydrocarbons such as benzene, napthalene and anthracene fluoresce fairly well or strongly in the near ultraviolet or visible spectral region, the corresponding aza-derivatives and carbonyl-derivatives are completely non-fluorescent or emit very weakly in spite of their comparable or stronger absorption intensity compared with the analogous aromatic hydrocarbons. In N-heterocyclics or carbonyl compounds, the lowest singlet-singlet transition has been characterized as a transition corresponding to the excitation of a non-bonding (nitrogen or oxygen) electron to an antibonding π molecular orbital. These transitions were designated as n→π* transitions, and their corresponding excited states as (n,π*) singlet states. As demonstrated by Kasha,²⁶ molecules with an (n,π*) state as their lowest excited singlet state are generally nonfluorescent because the properties of such a state are favorable for nonradiative deactivation. It is commonly accepted that this nonradiative deactivation occurs by an intercombination process which finally populates the lowest triplet state of the molecule. Such a crossing can result in emission from the triplet, or more generally in an absence of luminescence. Nitrogen heterocyclics possess both Π→Π* and n→π* transitions; in small ring compounds, the lowest singlet is

(n, π*) state. Most of these molecules show no fluorescence but have strong phosphorescences. El-Sayed\textsuperscript{27} has calculated that intersystem crossings between singlet and triplet states of the same configuration are forbidden in first order. He has suggested that $S (n, \pi^*) \rightarrow T (\pi, \pi^*)$ is the radiationless process which makes the intersystem crossing from the lowest (n, π*) singlet state of the nitrogen heterocycles very efficient. Complete examination of carbonyl compounds has not as yet been carried out. However, the existing data suggested that they resemble N-heterocycles in their behavior. Aromatic aldehydes and ketones, e.g. benzophenone and benzaldehyde, show strong phosphorescence but no fluorescence.\textsuperscript{28} In these systems, the triplet states of the aromatic ring might lie between the (n, π*) singlet and the triplet states of the carbonyl group. Aliphatic ketones and aldehydes, e.g. formaldehyde, show both fluorescence and phosphorescence. In these systems, the absence of a low (π, π*) triplet state retards the intersystem crossing process so that fluorescence competes successfully.\textsuperscript{29} Higher aromatic aldehydes are fluorescent.\textsuperscript{30} In benzaldehyde the n→π* absorption

\begin{footnotesize}
\textsuperscript{29}Lower, S. K. and M. A. El-Sayed, op. cit.
\end{footnotesize}
(0 - 0 band in heptane at 27.0 x 10^3 cm^{-1}) is well separated from the next π→π* absorption (0 - 0 band at 34.6 x 10^3 cm^{-1}) so that the (n, π*) singlet state is the lowest excited one in all reasonable solvents. Both kinds of states are shifted to lower energies in the higher members of the aromatic series, but, by their very nature, the (n, π*) states are shifted less than the (π, π*) states so that (π, π*) finally becomes the lowest singlet state and the higher aromatic aldehydes are therefore fluorescent. Solvent effects that shift the (π, π*) singlet state until it becomes the lowest excited singlet state have been observed in some aromatic aldehydes. In suitable molecules in inert solvents, the quenching (n, π*) state may be the lower, but the radiating (π, π*) state may be lower in other solvents. In inert solvents these molecules will be nonfluorescent, but fluorescence will occur in polar admixtures or in pure polar solvent.
II. Experimental

A. Compounds and Solvents:

Dibenzoylmethane was provided by Professor J. L. E. Erickson of the Department of Chemistry, Louisiana State University. Benzoylacetone, benzoyl trifluoroacetone, 2-bromo-1,3-diphenyl-1,3-propanedione, dibenzalacetone, were commercial products of Eastman Organic Chemicals. All of these compounds were purified by two or three recrystallizations from spectral grade isopropyl alcohol followed by vacuum sublimation.

Acetylacetone was obtained from Fisher Scientific Company, hexafluoroacetylacetone was obtained from Peninsular Chem Research Inc., and benzaldehyde was the product of Matheson Coleman and Bell. They were distilled before using.

Phillips pure grade isopentane and 3-methylpentane were washed by stirring them twice with fuming sulfuric acid for three hours. Then they were rinsed with water, saturated sodium carbonate solution and then water again. The solvents were dried over anhydrous magnesium sulfate for at least 24 hours and then distilled at the rate of 10 to 20 drops per minute. All hydrocarbon solvents showed no absorption at wavelengths greater than 210 nm. Cyclohexane and isopropyl alcohol were spectroquality reagents of Matheson Coleman and Bell. They were used without further purification.

Solvents used in the liquid nitrogen temperature (77°K) studies were 3-methylpentane, IPMP, a 6:1 mixture by volume of isopentane and 3-methylpentane, and EPA, a mixture by volume of 5 parts
isopentane, 5 parts ethyl ether and 2 parts of ethyl alcohol. EPA mixed solvent from Hartman Leddon Co. was used without further purification. All these solvents showed no emission and absorption in the wavelength range of interest and formed rigid glasses at liquid nitrogen temperature.

B. Spectral Measurement:

A Cary model 14 spectrophotometer produced by the Applied Physics Corporation was used to obtain the room temperature absorption spectra. The absorption spectra at 77°K were determined by the same instrument with the following modification: the cell holder in the sample compartment was removed and the sample compartment lid was replaced by a wood plate which provided support for the quartz dewar which contained liquid nitrogen. A Beckman standard 1 cm rectangular quartz absorption cell was suspended in the center of the dewar, namely, in the path of the light beam. The suspension of the sample cell in the path of the light beam was accomplished by means of a length of Pyrex rod which was fused to the ground glass stopper of the cell. The cell was held firmly to the stopper by a \( \frac{3}{4} \) inch length of tygon tubing which was split for half its length. The Pyrex rod was inserted in a cork stopper which fit firmly in the top of the dewar. The sample compartment was continually flushed with dry nitrogen gas to prevent the condensation of moisture on the dewar surface. When the low temperature absorption spectra were determined the instrument was run as a double beam instrument, but the
solvent in an identical Beckman 1 cm rectangular quartz cell at room temperature was used in the reference beam. Since the quartz dewar absorbed light below 245 μm, the absorption spectra were studied in the region above this wavelength. The absorbance values determined by this system were reproducible. The extinction coefficients in IPMP solvent at 77°K were obtained after the concentration of the sample was converted from its room temperature value to that at 77°K. The specific volume ratio of IPMP at 77°K and 293°K has been shown to be 0.76.31 This volume correction was the only one which was taken into consideration in the determination of the extinction coefficient at 77°K.

The irradiated species were obtained by irradiating the sample with the full intensity of a 1000 watts General Electric A-H6 high pressure mercury arc operated from an A.C. power supply.

At room temperature photoproducts were obtained by irradiating the samples in the empty dewar. In order to carry out the irradiation at 77°K, liquid nitrogen was added to the dewar. The species were kept in a rigid glass by adding liquid nitrogen to the dewar from time to time to keep the glass rigid all the time. A blower was used to prevent the condensation of the moisture on the outside surface of the dewar.

All emission spectra reported here were obtained from rigid

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glassy solutions at liquid nitrogen temperature, 77°K. The phosphorescence spectra were obtained by means of either an Aminco-Keirs spectrophosphorimeter produced by the American Instrument Co., or the Cary Model 14 spectrophotometer. The techniques of utilization of the Cary Model 14 to detect phosphorescence spectra have been described in detail by Harris and Williamson. A phosphoroscope was fitted flush to the back of the spectrophotometer after the visible light source, the tungsten lamp, was removed. The sample was approximately at the normal position of the tungsten lamp. The phosphoroscope was a double blade type which, by means of offset slits in co-axial disks, alternately exposed the sample to the exciting light source, a 1000 watts General Electric A-H6 high pressure mercury arc, and then as an emitting sample to the Cary spectrophotometer. The spectrophotometer was operated in the total energy, single beam reference mode, and the spectra were recorded by using the percent transmission slide wire. The apparatus arrangement for phosphorescence measurement by utilizing the Cary 14 spectrophotometer is shown in Figure 2 (a). All phosphorescence excitation spectra and the phosphorescence decay half lifes were obtained by means of the Aminco-Keirs spectrophosphorimeter. The excitation


source was a Xenon XBO 150 W lamp (Osram), and the detector was an RCA 1P28 photomultiplier tube. The phosphorescences and the phosphorescence excitation spectra were recorded with an Electro Instruments X-Y recorder. The phosphorescence decay was displayed on the screen of a Tektronix 585 oscilloscope and photographed.

The fluorescence emission spectra were recorded with the Cary Model 14 spectrophotometer to which a total emission apparatus was attached. The total emission apparatus, see Figure 2 (b), was designed to give front surface excitation. The monochromator used to isolate the desired exciting wavelength was a Cary Model 15 excitation monochromator. The excitation source was a Xenon XBO 450 W lamp (Osram). An aluminum tube was placed between the lamp compartment mounting plate and the monochromator to seal the monochromator from extraneous room light and the outside atmosphere. The U.V. filter (Corning #7910), which was located at the entrance of the light tube from the lamp compartment, was removed in order to permit operation in the U.V. region. In detecting the total emission spectra, the sample tube was placed at the position of the tungsten lamp of the Cary 14 spectrophotometer and the spectrophotometer was operated in the same mode as it was in detecting the phosphorescence spectra.
Figure 2. a. Apparatus Arrangement for Phosphorescence Measurement

Figure 2. b. Apparatus Arrangement for Total Emission Measurement
III. RESULTS AND DISCUSSION

The absorption spectra of benzoylacetone, benzoyl trifluoroacetone, dibenzoylmethane, 2-bromo-1,3-diphenyl-1,3-propanedione, and dibenzalacetone at room temperature in cyclohexane and in isopropyl alcohol are shown in Figure 3 and Figure 4, respectively. The wavelength and frequency of the absorption maximum and its molar extinction coefficient are given in Table 1 and Table 2. Most of the β-diketones exist mainly in the chelated enol form at room temperature. The formation of an intramolecular hydrogen bond in the chelated enol form stabilizes the molecule. The absorption spectra observed at room temperature are the spectra of the chelated enol tautomer of β-diketones. In the previous study,\textsuperscript{34} the longest wavelength band (usually above 285 μm) was assigned to the cinnamoyl chromophore and the band in the intermediate region (240 μm to 270 μm) was considered to be due to the presence of the benzoyl group in the molecule. The shortest wavelength band, which appears below 240 μm, has been assigned to be the result of an electronic transition due to the presence of the styrene like moiety. Most of the aromatic β-diketones have these three main bands in the ultraviolet region. 2-Bromo-1,3-diphenyl-1,3-propanedione is a β-diketone with the α-hydrogen substituted by a bromo group. It shows only one electronic transition in the ultraviolet region. The

\textsuperscript{34}Kuo, J., op. cit.
Figure 3. Absorption Spectra in Cyclohexane at Room Temperature

a. Benzoylacetone  
\( \text{C}_6\text{H}_5\text{C(OH):CHCOCH}_3 \)

b. Benzoyl trifluoroacetone  
\( \text{C}_6\text{H}_5\text{C(OH):CHCOCF}_3 \)

c. Dibenzoylmethane  
\( \text{C}_6\text{H}_5\text{C(OH):CHCOC}_6\text{H}_5 \)

d. 2-Bromo-1,3-diphenyl-1,3-propanedione  
\( \text{C}_6\text{H}_5\text{COHBrCOC}_6\text{H}_5 \)

e. Dibenzalacetone  
\( \text{C}_6\text{H}_5\text{CH:CHCOCH:CHO}_6\text{H}_5 \)
Figure 4. Absorption Spectra in Isopropyl alcohol at Room Temperature

a. Benzoylacetone
b. Benzoyl trifluoroacetone
c. Dibenzoylmethane
d. 2-Bromo-1,3-diphenyl-1,3-propanedione
e. Dibenzalacetone
Table 1. Absorption Spectra in Cyclohexane at Room Temperature

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\bar{\nu}$ (cm$^{-1}$)</th>
<th>$\epsilon$</th>
<th>log $\epsilon$</th>
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<tr>
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<td>29800</td>
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<td></td>
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<td>44400</td>
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<td>43100</td>
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Table 2. Absorption Spectra in Isopropyl alcohol at Room Temperature

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<th>Compounds</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\epsilon$</th>
<th>$\log \epsilon$</th>
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<td>230</td>
<td>43500</td>
<td>5.65 x 10$^3$</td>
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longest wavelength band and the shortest wavelength band are missing from the spectra. This can be explained by the fact that 2-bromo-1,3-diphenyl-1,3-propanedione exists mainly in the keto form at room temperature. The absorption spectra of dibenzalacetone, which is not a β-diketone, are also shown for comparison. It absorbs light in the region above 285 μm and at the region below 240 μm. There is no absorption band corresponding to the benzoyl chromophore band. Since there is no benzoyl group in the dibenzalacetone molecule, the molecule is not expected to have a transition in the region between 240 μm and 270 μm.

The longest wavelength bands of β-diketones shift to the red as the solvent changes from cyclohexane to isopropyl alcohol. In dibenzoylmethane the shift is from 336 μm (29800 cm\(^{-1}\)) to 340 μm (29400 cm\(^{-1}\)) and the amount of the shift is 400 cm\(^{-1}\). The shifts of benzoylacetone, benzoyltrifluoroacetone and dibenzalacetone are 300 cm\(^{-1}\), 200 cm\(^{-1}\) and 400 cm\(^{-1}\), respectively. The intermediate wavelength bands of dibenzoylmethane, benzoyltrifluoroacetone, and 2-bromo-1,3-diphenyl-1,3-propanedione do not change as the solvent is changed from cyclohexane to isopropyl alcohol, while the corresponding band of benzoylacetone has a red shift of 100 cm\(^{-1}\). The solvent effects on the shortest wavelength bands are more complicated. The shortest wavelength band of dibenzoylmethane is not shifted by the solvent. In benzoyltrifluoroacetone and dibenzalacetone, they shift to the red for 1500 cm\(^{-1}\) and 200 cm\(^{-1}\), respectively as
the solvent varies from hydrocarbon to alcohol. On the contrary the corresponding band in benzoylacetonite is blue shifted 400 cm\(^{-1}\) from the cyclohexane solvent to the isopropyl alcohol solvent. From the behavior of the absorption band upon change of the solvent and their molar extinction coefficients, which have values higher than 5000, we conclude that all the observed transitions are \(\pi \rightarrow \pi^*\). The weak \(n \rightarrow \pi^*\) transitions must be hidden under the much stronger \(\pi \rightarrow \pi^*\) transitions and they can not be detected.

In a series of papers, Nagakura et al.\(^{35-37}\) have developed a theory of intramolecular charge transfer. According to these authors, in molecules or ions in which electron donating and accepting groups combine with each other directly or through a bridge of conjugated double bonds, electron transfer takes place easily between the groups and strong bands characteristic of the interaction between the two groups appear. This kind of band is called an intramolecular charge transfer band. They have applied this theory to the interpretation of 285 nm band of benzalacetone in alcohol. This transition has been suggested to be the result of the migration of a \(\pi\)-electron in the highest occupied \(\pi\)-level of styrene, which acts as a donor,

\[^{36}\text{Nagakura, S., J. Chem. Phys. 23 1441 (1955).}\]
\[^{37}\text{Hashimoto, F., J. Tanaka and S. Nagakura, J. Mol. Spectry. 10 401 (1963).}\]
into the lowest vacant π-orbital of acetone, which is an acceptor, and the excitation energy corresponding to the ultraviolet absorption is given by

$$E_{\text{excit.}} = \left[ (H_x - V_a)^2 - 4 \, C_x^2 \, C_a^2 \, p^2 \right]^{1/2}$$

(1)
in which $H_x$ and $V_a$ are energies of the highest occupied π-orbital of styrene and of the lowest vacant π-orbital of acetone, respectively. $C_x$ is the coefficient of the atomic orbital of the carbon atom of the styrene (with the highest π-orbital occupied) to which the acetone is attached, and $C_a$ is the coefficient of the atomic orbital of the acetone (with the lowest π-orbital vacant) to which the styrene is attached. $p$ is the exchange integral between the carbon atoms linking the styrene and acetone. We can apply this theory to the interpretation of the longest wavelength bands in β-diketones. The donor and the acceptor for each molecule and the corresponding intramolecular charge transfer band are given in Table 3. For the same donor, the intramolecular charge transfer band shifts to the red as the acceptor is varied from acetone to acetophenone. This conclusion was reached by comparing the intramolecular charge transfer bands between the pairs of benzalacetone and benzalacetophenone, and benzoylacetonc and dibenzoylmethane. In the former the donor group for both molecules is styrene, while the acceptor for benzalacetone is acetone and the acceptor for benzalacetophenone is acetophenone. The intramolecular charge transfer band of benzalacetophenone is red-shifted compared with that of
Table 3. Intramolecular Charge Transfer Bands

<table>
<thead>
<tr>
<th>Compound</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Absorption Maximum, µm</th>
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<tbody>
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<td></td>
<td></td>
<td>in H.C.</td>
<td>in alc.</td>
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<tr>
<td>( \text{C}_6\text{H}_5\text{CH} : \text{CHCOCH}_3 )</td>
<td>( \text{C}_6\text{H}_5\text{CH} : \text{CH}_2 )</td>
<td>( \text{CH}_3\text{COCH}_3 )</td>
<td>279*</td>
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<td>Benzalacetone</td>
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<tr>
<td>( \text{C}_6\text{H}_5\text{CH} : \text{CHOOC}_6\text{H}_5 )</td>
<td>( \text{C}_6\text{H}_5\text{CH} : \text{CH}_2 )</td>
<td>( \text{CH}_3\text{COCC}_6\text{H}_5 )</td>
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<td>Benzalacetophenone</td>
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<td>( \text{C}_6\text{H}_5\text{C(OH)} : \text{CH}_2 )</td>
<td>( \text{CH}_3\text{COCC}_6\text{H}_5 )</td>
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<td>Dibenzoylmethane</td>
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<td>( \text{C}_6\text{H}_5\text{C(OH)} : \text{CH}_2 )</td>
<td>( \text{CH}_3\text{COCH}_3 )</td>
<td>305</td>
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<td></td>
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<tr>
<td>( \text{CH}_3\text{C(OH)} : \text{CHOCC}_6\text{H}_5 )</td>
<td>( \text{CH}_3\text{C(OH)} : \text{CH}_2 )</td>
<td>( \text{CH}_3\text{COCH}_3 )</td>
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<tr>
<td>Acetylacetone</td>
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<tr>
<td>( \text{CF}_3\text{C(OH)} : \text{CHOCCF}_3 )</td>
<td>( \text{CF}_3\text{C(OH)} : \text{CH}_2 )</td>
<td>( \text{CH}_3\text{COCF}_3 )</td>
<td>272</td>
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<tr>
<td>Hexafluoroacetylacetone</td>
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<td></td>
<td></td>
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<tr>
<td>( \text{C}_6\text{H}_5\text{C(OH)} : \text{CHOCCF}_3 )</td>
<td>( \text{C}_6\text{H}_5\text{C(OH)} : \text{CH}_2 )</td>
<td>( \text{CH}_3\text{COCF}_3 )</td>
<td>323</td>
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<tr>
<td>Benzoyl trifluoroacetone</td>
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*Data from J. Kuo's M.S. Thesis, Louisiana State University, Baton Rouge, Louisiana (1963)
benzalacetone. The intramolecular charge transfer band of dibenzoyl methane is red-shifted compared with that of benzoylacetone. They have the same donor group, C₆H₅C(OH):CH₂, while the acceptor for benzoylacetone is acetone and the acceptor for dibenzoylmethane is acetophenone. The acceptor group of CH₃COCHF₂ causes the intramolecular charge transfer band of benzoyl trifluoroacetone, which has C₆H₅C(OH):CH₂ as an acceptor, to fall between that of benzoylacetone and dibenzoylmethane. By comparing the intramolecular charge transfer bands of acetylacetone, benzalacetone and benzoylacetone, it is found that they shift to the red as the donor groups vary from CH₃C(OH):CH₂ to C₆H₅CH:CH₂ and to C₆H₅C(OH):CH₂, while the acceptor group in all the three molecules is acetone. Hexafluoroacetylacetone and benzoyl trifluoroacetone have trifluoro-acetone as an acceptor, while the former has CF₃C(OH):CH₂ as a donor and the latter has C₆H₅C(OH):CH₂ as a donor. The difference in the donor group causes that the intramolecular charge transfer band of benzoyl trifluoroacetone to shift to the red from that of hexafluoroacetylacetone. β-Diketones in the enol-form can have this intramolecular charge transfer band. This transition can not occur in the keto form of β-diketones because of the lack of the conjugated system in the molecule. This is a criterion for distinguishing the enolic β-diketone from the β-diketone in the keto form.

The absorption spectrum of dibenzoylmethane in isopropyl alcohol has been measured at different concentrations. The absorption spectra
are identical in each case, all having absorption maxima at 340 μm, 250 μm and 225 μm. This is an evidence of the existence of an intramolecular hydrogen bond in dibenzoylmethane. Because of this hydrogen bond, increasing ionization of dibenzoylmethane does not occur upon dilution, and, hence there is no change in the spectrum. The same situation is found in benzoylaceton and benzoyltrifluoroacetone. The absorbance vs. concentration curve for dibenzoylmethane in isopropyl alcohol for each absorption maximum is given in Figure 5. All give a straight line which indicates that Beer's law is followed; consequently, no dimerization or other chemical reactions take place in the concentrated solutions. The same curves have been obtained after the solution is subjected to irradiation by ultraviolet light at room temperature. Photodecomposition or photopolymerization does not occur in dibenzoylmethane when it is irradiated at room temperature. The highest concentration of dibenzoylmethane in this study is higher than all the concentrations in the studies described herein. Therefore it can be assumed that there is no photopolymerization in this study.

When dry hydrogen chloride gas was bubbled into the isopropyl alcohol solution of dibenzoylmethane, the intramolecular charge transfer band remained in the same position with a slight decrease in intensity while the absorption band of intermediate wavelength shifted to the red with a substantial increase in the intensity (see Figure 6). The band is broader and less symmetric after hydrogen
Figure 5. Absorbance vs. Concentration of Dibenzoylmethane in Isopropyl alcohol

a. 340 mm Peak
b. 250 mm Peak
c. 225 mm Peak
Figure 6. Absorption Spectra of Dibenzoylmethane in Isopropyl alcohol at Room Temperature
a. before Addition of HCl
b. after Addition of HCl for 3 mins.
c. after Addition of HCl for 5 mins.
chloride gas is bubbled into the solution. It is suspected that this band results from an overlapping of two closely spaced bands. The intensity of the band at the longer wavelength side increases when hydrogen chloride is added, while the intensity of the band at the shorter wavelength side decreases or remains the same. As a result the summation of effects causes the observed band shifts to the red and broadens the band width. The separation of these two bands seems to be in the neighborhood of 20 µm. The shorter wavelength band has its maximum at around 255 µm and the maximum of the longer wavelength band is in the region of 270 µm. Before hydrogen chloride gas is added the shorter wavelength band is predominant. After hydrogen chloride gas is added the intensity of the longer wavelength band increases. Finally the longer wavelength band overtakes the shorter wavelength band and the former becomes the main contributor to the observed band. The slight decrease in the intensity of the intramolecular charge transfer band suggests that the enol tautomer decreases when hydrogen chloride gas is bubbled into the dibenzoylmethane in isopropyl alcohol. The 255 µm band is assigned to the second \( \pi \rightarrow \pi^* \) transition of the enolic tautomer of dibenzoylmethane, and the band in the region of 270 µm is assigned to the keto tautomer of the dibenzoylmethane. This assignment is based on the blue phosphorescence excitation spectrum of dibenzoylmethane in EFA, which has a transition at 273 µm. The observed spectral change upon the addition of hydrogen chloride gas to the isopropyl alcohol solution of
dibenzoylmethane can be explained to be that resulting from the displacement of the keto–enol equilibrium towards the keto form. We can consider the keto–enol tautomeric equilibrium in solution to be an acid-base equilibrium of two acids—the keto and enol forms which yield by ionization, the same, common anion of enolate structure. Proton transfer from enol to keto and back is affected by the participation of proton-carrier molecules $S$, which can unite reversibly with a proton,

$$
EH + S \rightleftharpoons E^- + HS^+ \rightleftharpoons KH + S
$$

in which $EH$ and $KH$ are the enol and the keto tautomers and $E^-$ is the anion. The part of the proton carriers may be played by any species having an affinity for a proton. They can be solvent molecules, e.g. isopropyl alcohol, ethyl alcohol and ether in EPA, or the molecules of the keto–enol themselves. Normally one would expect that the enol tautomer has a higher acid dissociation constant that the keto tautomer. This is true in the case of the unchelated enol. In the case of the chelated enol the keto form is expected to be stronger acid than the enol form. This results from the presence in the enol form of an intramolecular hydrogen bond, which stabilizes the undissociated enol molecule. Addition of protons displaces the equilibrium toward the keto tautomer.

The intramolecular charge transfer bands have been studied further at liquid nitrogen temperature, $77^\circ K$. The substances were dissolved either in IPMP or EPA which form transparent rigid glasses
Figure 7. Absorption Spectra of Dibenzoylmethane in IPMP

- a. at 25°C
- b. at 77°K
- c. at 77°K after Irradiation with the A-H6 for 60 mins.
- d. at 25°C after Irradiation at 77°K.
Figure 8. Absorption Spectra of Dibenzoylmethane in EPA
   a. at 25°C
   b. at 77°C
   c. at 77°C after Irradiation with the A-H6 for 60 mins.
at 77°K. The intramolecular charge transfer band of dibenzoylmethane in IPMP is given in Figure 7. At room temperature it shows a broad band with the maximum at 335 μm (29850 cm⁻¹) and two shoulders at 295 μm (33900 cm⁻¹) and 365 μm (27400 cm⁻¹) in the ultraviolet region. As the temperature decreases to the liquid nitrogen temperature, 77°K, the band shifts to the red and three distinct vibrational bands with maxima at 379 μm (26390 cm⁻¹), 362 μm (27620 cm⁻¹) and 350 μm (28570 cm⁻¹) appear. The observed vibrational frequencies in the first excited singlet state are 1230 cm⁻¹ and 950 cm⁻¹. The 362 μm vibrational band has the greatest intensity. The 0–0 band, which is the transition between the 0th vibrational levels of the ground state and the first excited singlet state or the vibrational band with the longest wavelength maximum, occurs at 379 μm. According to the Franck-Condon principle, if the first excited singlet state and the ground state have significantly different geometries, the 0–0 band may not be the band of maximum intensity. The intramolecular hydrogen bond is the main factor which causes the different geometries in the ground and the first excited singlet states. In the EPA solvent at room temperature, the intramolecular charge transfer band of dibenzoylmethane has a maximum at 340 μm (29410 cm⁻¹) with shoulders at 295 μm, 330 μm and 365 μm. Four vibrational structures with maxima at 378 μm (26460 cm⁻¹), 359 μm (27860 cm⁻¹), 344 μm (29070 cm⁻¹), and 300 μm (33330 cm⁻¹) appear at 77°K as shown in Figure 8. The observed vibrational frequencies are 4260 cm⁻¹,
Figure 9. Absorption Spectra of Benzoylacetone in IPMP

a. at 25°C
b. at 77°K
c. at 77°K after Irradiation with the A-H6 for 60 mins.
d. at 25°C after Irradiation at 77°K
Figure 10. Absorption Spectra of Benzoylaceton in EPA

a. at 25°C
b. at 77°K
c. at 77°K after Irradiation with the A-H6 for 60 mins.
1210 cm$^{-1}$ and 1400 cm$^{-1}$. The band of the maximum intensity is the longest wavelength band, 378 μm, namely the 0-0 band. This means that the geometries of the excited state and the ground state of dibenzoylmethane in EPA are not much different.

Intramolecular charge transfer bands of benzoylacetone in IPMP and in EPA are shown in Figures 9 and 10, respectively. In IPMP at room temperature it shows a broad band with a maximum at 304 μm (32890 cm$^{-1}$) and shoulders around 320 μm and 345 μm. This band shifts to the red at 77°K and shows five vibrational bands at 350 μm (28570 cm$^{-1}$), 334 μm (29940 cm$^{-1}$), 320 μm (31250 cm$^{-1}$), 310 μm (32260 cm$^{-1}$) and 300 μm (33330 cm$^{-1}$). The observed vibrational frequencies are 1370 cm$^{-1}$, 1310 cm$^{-1}$, 1010 cm$^{-1}$ and 1070 cm$^{-1}$. The band of maximum intensity is the 320 μm band. In EPA at room temperature the intramolecular charge transfer band of benzoylacetone is an unsymmetric one with a tail on the long wavelength side and with an absorption maximum at 305 μm (32790 cm$^{-1}$). The corresponding vibrational bands at 77°K are at 346 μm (28900 cm$^{-1}$), 330 μm (30300 cm$^{-1}$), 318 μm (31450 cm$^{-1}$), 308 μm (32470 cm$^{-1}$) and 298 μm (33560 cm$^{-1}$). The observed vibrational frequencies are 1310 cm$^{-1}$, 1150 cm$^{-1}$, 1020 cm$^{-1}$ and 1090 cm$^{-1}$.

Benzoyltrifluoroacetone spectra are similar to those of benzoylaceton. In IPMP at room temperature the intramolecular charge transfer band of benzoyltrifluoroacetone has an absorption maximum at 322 μm (31060 cm$^{-1}$) and a shoulder at 300 μm (33330 cm$^{-1}$). At 77°K
Figure 11. Absorption Spectra of Benzoyl-trifluoroacetone in IPMP

a. at 25°C

b. at 77°K

c. at 77°K after Irradiation with the A-H6 for 60 mins.

d. at 25°C after Irradiation at 77°K
Figure 12. Absorption Spectra of Benzoyl-trifluoroacetone in EPA

a. at 25°C
b. at 77°C

c. at 77°C after Irradiation with the A-H6 for 60 mins.
vibrational bands appear at 356 μ (28090 cm$^{-1}$), 338 μ (29590 cm$^{-1}$), 328 μ (30490 cm$^{-1}$) and 305 μ (32790 cm$^{-1}$) as shown in Figure 11. In EPA at room temperature the absorption maximum of this band is at 324 μ (30860 cm$^{-1}$), while at 77°K this charge transfer band shows vibrational structures with the maxima at 358 μ (27930 cm$^{-1}$), 339 μ (29500 cm$^{-1}$), 328 μ (30490 cm$^{-1}$) and a shoulder around 312 μ (32050 cm$^{-1}$). The observed vibrational frequencies of the first excited singlet state of benzoyl trifluoroacetone at 77°K are 1500 cm$^{-1}$, 900 cm$^{-1}$ and 2300 cm$^{-1}$ at IPMP and they are 1530 cm$^{-1}$ and 990 cm$^{-1}$ at EPA.

The temperature dependent change in the absorption spectra has been suggested to result from a temperature effect on the refractive index of a solvent, a temperature effect on the Boltzmann distribution among vibrational and rotational energy levels of the solute molecule, and temperature-dependent interactions of the molecules in the system. The temperature-dependence of the IPMP and EPA solvents does not change the absorption spectra substantially; this has been demonstrated by Williamson. The temperature-dependence of the vibrational and rotational energy levels can be interpreted in terms of the Franck-Condon principle. In view of the spectral width of the bands at room temperature, it is evident that

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39Williamson, H. L., op. cit.
they contain more than a single vibrational transition. They are superpositions of numerous vibrational bands, all of which belong to the same electronic transition, smeared into a continuous band by the action of the fields of neighboring molecules. These vibrational transitions involve changes in the quantum numbers of several normal vibrations. As the temperature rises, the light absorbing molecules are raised into higher vibrational quantum states, in accord with the Boltzmann distribution law. The most probable transitions for these molecules involve, by the Franck-Condon principle, different changes of vibrational quantum numbers from those of molecules in the lowest level. The superposition of all these transitions must result in a broadening and flattening of the over-all absorption curve. Therefore, absorption band sharpness increases and position of absorption maximum does not shift or shifts very little to the longer wave length side with decreasing temperature. In our case the band sharpness does increase and vibrational structure appears as the temperature decreases to \(77^\circ\text{K}\) and the position of the absorption maximum does shift to the longer wavelength side a substantial amount. This shift must be caused by the formation of more intramolecular hydrogen bond at the low temperature.

The red-shift of the absorption spectrum upon the formation of an intramolecular hydrogen bond can be interpreted by the intramolecular charge transfer theory and by the Franck-Condon principle. According to the intramolecular charge transfer model the excitation
energy is dependent on $H_x$, $V_a$, $C_x$, $C_a$ and $\beta$ (see Equation (1)).

This excitation energy depends on the value of $C_a$ if the other quantities are constant. A decrease in the $C_a$ value is correlated with a red shift in the absorption spectrum. This occurs in a molecule upon the formation of an intramolecular hydrogen bond between the C=0 and OH groups. In the course of formation of an intramolecular hydrogen bond, charge distribution in the carbonyl group must be greatly affected and the contribution of ionic forms $\bar{O} - \bar{H}$ and $\bar{C} - \bar{O}$ to the bond resonance is increased; consequently the electrostatic attraction between the positively charged hydrogen atom of the OH group and the negatively charged oxygen atom of the C=0 group increases. As a result the carbon atom of the carbonyl group becomes more positive on the formation of an intramolecular hydrogen bond. This decreases the $C_a$ value and causes that the intramolecular charge transfer band to shift to the red. Pimentel\textsuperscript{40} has interpreted the spectrum change upon the formation of a hydrogen bond in terms of the Franck-Condon principle. The spectrum change is dependent on the difference of the energy of the hydrogen bond in the excited state of the molecule and the energy of the hydrogen bond in the ground state of the molecule. The absorption spectrum shifts to the red if the energy of the hydrogen bond in the excited state of the molecule is higher than that in the ground state of the molecule.

\textsuperscript{40}Pimentel, G. C., J. Am. Chem. Soc. \textbf{79} 3323 (1957).
The observed absorption spectra of benzoylacetone, benzoyl-
trifluoroacetone, acetylacetone and dibenzoylmethane remain unchang-
ed when they are irradiated with the full intensity of the A-H at
room temperature. The absorption spectra in both IPMP and EPA at
room temperature are the same before and after the irradiation. This
indicates that either there are no photochemical reactions at room
temperature or that the photoreaction products are highly unstable
and convert to the original molecules by losing energy through ther-
mal collision with the solvent molecules as soon as they form. The
lack of observed photochemical reactions in these compounds can be
attributed to the presence of the intramolecular hydrogen bond in
these molecules.

The absorption spectra of 2-bromo-1,3-diphenyl-1,3-pro-
panedione in either hydrocarbon or alcohol at room temperature are
different before and after the irradiation. In hydrocarbon the ab-
sorption spectrum of 2-bromo-1,3-diphenyl-1,3-propanedione has an
absorption maximum at 253 μu before irradiation; after irradiation
the intensity of the 253 μu peak decreases and two absorption bands
with maxima at 330 μu and 229 μu appear. The same thing happens in
the alcoholic solvent; before irradiation, the absorption maximum is
at 253 μu with a shoulder around 275 μu, and after irradiation two
absorption maxima at 340 μu and 225 μu appear and the original 253
μu peak becomes a shoulder in the spectrum. The evidence indicates
that 2-bromo-1,3-diphenyl-1,3-propanedione exists mainly in the keto
form at room temperature. Upon irradiation the keto-enol equilibrium
Figure 13. Absorption Spectra in IPMP at Room Temperature

a. 2-Bromo-1,3-diphenyl-1,3-propanedione
b. 2-Bromo-1,3-diphenyl-1,3-propanedione after Irradiation at 25°C
c. Dibenzoylmethane
Figure 14. Absorption Spectra in IPMP at 77°K

a. Dibenzoylmethane

b. Irradiated 2-Bromo-1,3-diphenyl-1,3-propanedione

c. Irradiated Dibenzoylmethane.
is displaced towards the enol tautomer. The presence of the intramolecular charge transfer band and the band below 230 μm indicates the presence of the enol tautomer in the irradiated molecule. A comparison of the absorption spectra of dibenzoylmethane, 2-bromo-1,3-diphenyl-1,3-propanedione, and the irradiated 2-bromo-1,3-diphenyl-1,3-propanedione in IPMP at room temperature is shown in Figure 13. The intramolecular charge transfer bands of these molecules at 77°K are shown in Figure 14. Except for the intensity, the absorption spectrum of the irradiated 2-bromo-1,3-diphenyl-1,3-propanedione is almost identical with the absorption spectrum of dibenzoylmethane.

The observed absorption spectra of β-diketones are different before and after irradiating the molecules at 77°K. At 77°K, the intramolecular charge transfer band of the molecules is blue shifted and its intensity decreases after irradiation. (see Figures 7 through 12). The decrease in the intensity and the degree of the blue-shift of the absorption maximum of the intramolecular charge transfer band at 77°K is proportional to the time of the irradiation. The longer the molecule at 77°K is exposed to the A-H6 light the lower the intensity of the intramolecular charge transfer band and the more the band maximum shifts to the blue. Two examples are shown in Figures 15 and 16 for the IPMP solutions of dibenzoylmethane and acetylacetone, respectively. In acetylacetone, the absorption maximum at 77°K is 277 μm before irradiation. After irradiation for 10 minutes the absorption maximum shifts to 268 μm and its intensity is very close to the intensity of the absorption band at room
Figure 15. Absorption Spectra of Dibenzoylmethane in IP!P at 77°K

a. before Irradiation
b. after Irradiation with the A-H6 for 15 mins.
c. after Irradiation with the A-H6 for 25 mins.
d. after Irradiation with the A-H6 for 35 mins.
e. after Irradiation with the A-H6 for 60 mins.
Figure 16. Absorption Spectra of Acetylacetone in IPMP

a. at $25^\circ$C
b. at $77^\circ$K before Irradiation
c. at $77^\circ$K after Irradiation with the A-H6 for 10 mins.
d. at $77^\circ$K after Irradiation with the A-H6 for 30 mins.
temperature, which has an absorption maximum at 269 mu. Further ir-
radiation for 20 minutes shifts the absorption maximum to 264 mu and
its intensity to lower than that of the band at room temperature.
The spectra of the molecules at room temperature before irradiation
and the spectra of the irradiated molecules at room temperature are
different. The latter were taken after irradiating the samples with
the A-H6 for 60 minutes at 77°K and then warming them to room temper-
ature. The intensity of the intramolecular charge transfer bands of
the irradiated molecules is lower than that of the molecules before
irradiation as shown in Figures 7, 9 and 11. The ratio of the in-
tensities of the intermediate wavelength band and of the intramolec-
ular charge transfer band in the irradiated molecule is larger than
that of the same molecule before irradiation.

Photochemical reactions took place upon irradiation of the
molecule in the rigid glass solvent at 77°K. The spectra of the mol-
ecules in the rigid glass were recorded from the region of visible
light into the region of infrared, 1500 mu. The spectra of the
region above 400 mu do not change upon irradiation. No trapped free
electron, which absorbs light in the region of near infrared, has
been detected. Photooxidation of the molecule in the rigid glass
upon irradiation by ejecting an electron does not occur in these
systems. This can be supported further by the observation of the
change in the absorption spectrum of the original molecule and the ir-
radiated molecule at room temperature. In a photoelectron ejection
reaction the ejected electron should recombine with the radical, which is formed initially by photooxidation of the original molecule, on raising the temperature to room temperature and the original molecule should be restored. That means that the original spectrum is restored by softening the glass, which is not the case observed in this work. The impossibility of the photoejection reaction in β-diketones can be attributed to the presence of the intramolecular hydrogen bond in these molecules. The formation of an intramolecular hydrogen bond ties down the lone pair electrons of the oxygen atom in the molecule and prohibits the oxidation reaction from occurring easily. It has already been mentioned that photopolymerization does not occur in these systems. The blue shift of the intramolecular charge band upon irradiation verifies this assumption further. It is unlikely that photodecomposition occurs upon irradiation of β-diketones in the rigid glass. This is supported by the facts that although the intensity of the spectrum of the original molecule and that of the irradiated molecule at room temperature are different, the positions of their absorption maxima are the same. If there were permanent photodecomposition products the absorption maxima of the irradiated products should shift to the blue with respect to that of the original molecule.

In order to study the photoreactions of β-diketones in the rigid glasses more thoroughly, luminescences of these compounds in the rigid glass have been investigated. Neither phosphorescence nor
fluorescence spectra of β-diketones have been observed at room temperature. At 77°K, all β-diketones studied in this work gave observable phosphorescences. β-Diketones in EPA glass give blue phosphorescences as soon as the exciting light, the full intensity of the A-H6, impinged upon the sample. They show another phosphorescence in the region around 500 μm but these phosphorescences are very weak.

The blue phosphorescence spectra of some β-diketones in EPA are given in Figure 17. The blue phosphorescence of dibenzoylmethane in EPA has four vibrational bands at 475 μm (21000 cm⁻¹), 440 μm (22700 cm⁻¹), 407 μm (24600 cm⁻¹) and 380 μm (26300 cm⁻¹). The band of maximum intensity is the 407 μm band. This phosphorescence decayed exponentially with a half life of 3.2 x 10⁻² sec. The observed vibrational frequencies of the ground state of dibenzoylmethane are 1700 cm⁻¹, 1900 cm⁻¹ and 1700 cm⁻¹. The blue phosphorescence of benzoylaceton decayed exponentially with a half life time of 3.0 x 10⁻² sec. and its spectrum has an intensity maximum at 415 μm, the band of shortest wavelength being at 390 μm. The observed vibrational frequencies of benzoylaceton are 1700 cm⁻¹, 1400 cm⁻¹ and 1500 cm⁻¹. The half life times of the blue phosphorescences of benzoyltrimfluoroacetone and of 2-bromol,3-diphenyl-1,3-propanedione are 1.2 x 10⁻³ sec. and 2.5 x 10⁻³ sec., respectively. The blue phosphorescence spectrum of benzoyltrimfluoroacetone has vibrational bands at 490 μm (20410 cm⁻¹), 455 μm (22000 cm⁻¹), 425 μm (23500 cm⁻¹) and 400 μm (25000 cm⁻¹) with the 425 μm being the band of maximum intensity.
Figure 17. Blue Phosphorescence Spectra in EPA
a. Dibenzoylmethane
b. Benzoylaceton
c. Benzoyltrifluoroacetone
d. 2-Bromo-1,3-diphenyl-1,3-propanedione
e. Benzaldehyde
The observed vibrational frequencies are 1590 cm\textsuperscript{-1}, 1500 cm\textsuperscript{-1} and 1500 cm\textsuperscript{-1}. Two peaks at 430 μm (23260 cm\textsuperscript{-1}) and 407 μm (24570 cm\textsuperscript{-1}) and a shoulder at 460 μm (21740 cm\textsuperscript{-1}) appear in the blue phosphorescence spectrum of 2-bromo-1,3-diphenyl-1,3-propanedione in EPA glass.

The observed vibrational frequencies are at 1520 cm\textsuperscript{-1} and 1310 cm\textsuperscript{-1}. The 430 μm band is the band of maximum intensity. The phosphorescence spectrum of benzaldehyde in EPA is shown in Figure 17 for comparison. It gives four vibrational bands at 473 μm (21120 cm\textsuperscript{-1}), 453 μm (22100 cm\textsuperscript{-1}), 422 μm (23700 cm\textsuperscript{-1}) and 394 μm (25360 cm\textsuperscript{-1}) with vibrational frequencies of 980 cm\textsuperscript{-1}, 1600 cm\textsuperscript{-1} and 1660 cm\textsuperscript{-1}. The 422 μm band is the band of maximum intensity. The phosphorescences in the region around 500 μm are so weak that measurement of their half lifes was not possible. Green phosphorescences can be observed after the sample glasses were removed from the exciting light, but not the blue phosphorescences. It is possible that the green phosphorescence has a longer half life than the blue phosphorescence.

When a selected wavelength of the exciting light is used, the green phosphorescence of β-diketones in EPA can be measured independently. These phosphorescence spectra were obtained by means of the Aminco-Keirs spectrophosphorimeter. The exciting wavelength, which is at wavelength greater than 300 μm, is the wavelength of the vibrational band of the intramolecular charge transfer band. With this low energy excitation no blue phosphorescence was observed in the spectrum, the only phosphorescence present in the spectrum was the green
Figure 13. Green Phosphorescence Spectra in EPA Exciting at the Intramolecular Charge Transfer Band

a. Dibenzoylmethane
b. Benzoylacetone
c. Benzoyltrifluoroacetone
phosphorescence. These green phosphorescences of β-diketones in EPA are shown in Figure 18. When dibenzoylmethane in EPA was subjected to an exciting light of 359 μm, it showed a green phosphorescence with vibrational structures at 527 μm (18980 cm⁻¹) and 490 μm (20410 cm⁻¹). The observed vibrational frequency is 1430 cm⁻¹. The 490 μm peak is the band of maximum intensity. Benzoylacetonate and benzoyltrifluoroacetone in EPA gave green phosphorescence when irradiated with light of 318 μm and 339 μm respectively. The green phosphorescence of benzoylacetonate has vibrational peaks at 495 μm (20200 cm⁻¹) and 464 μm (21550 cm⁻¹) with vibrational frequency of 1350 cm⁻¹. Vibrational structures of 485 μm (20620 cm⁻¹) and 455 μm (21980 cm⁻¹) with vibrational frequency of 1360 cm⁻¹ make up the green phosphorescence spectrum of benzoyltrifluoroacetone in EPA. Green phosphorescence has not been observed from 2-bromo-1,3-diphenyl-1,3-propanedione in EPA.

In the hydrocarbon glass β-diketones give initially a green phosphorescences in a very weak blue phosphorescences. The intensity of the blue phosphorescences builds up gradually, while the intensity of the green phosphorescence decreases slightly with time. Because of the small solubilities of β-diketones in hydrocarbon, the determination of half life of phosphorescences of β-diketones in this solvent fails. When the exciting light was in the region of the intramolecular charge transfer band, no blue phosphorescence has been observed but only the green phosphorescence can be observed from the
β-diketones either before or after irradiation. The irradiated β-
diketones in the hydrocarbon glass gave a strong blue phosphorescence
when they are excited with the full intensity of the A-H6. In 3-
methylpentane the irradiated dibenzoylmethane gives a blue and a
green phosphorescences. The green phosphorescence with vibrational
bands at 530 μm (18870 cm⁻¹) and 497 μm (20120 cm⁻¹) is weaker than
the blue phosphorescence which has vibrational bands at 452 μm (22120
cm⁻¹), 421 μm (23750 cm⁻¹) and 393 μm (25450 cm⁻¹). The vibrational
band, which corresponds to the 475 μm band of the blue phosphoresc­
ce in EPA, is submerged in the green phosphorescence and cannot
be found.

The phosphorescences of dibenzoylmethane in 3-methylpentane
are displaced toward longer wavelengths in comparison with the phos­
phorescences of the compound in EPA; this is shown in Figure 19.
Solvents affect the blue and the green phosphorescences differently.
The shortest wavelength band of the blue phosphorescence shifts from
393 μm (25450 cm⁻¹) to 380 μm (26300 cm⁻¹) as the solvent varies from
3-methylpentane to EPA. The shift caused by the difference in sol­
vents is 950 cm⁻¹. The shortest wavelength band of the green phos­
porescence shifts from 497 μm (20120 cm⁻¹) to 490 μm (20410 cm⁻¹) as
the solvent varies from 3-methylpentane to EPA. The amount of the
shift from 3-methylpentane to EPA is 290 cm⁻¹, which is about three
times less than the shift of the blue phosphorescence.

Phosphorescences of benzoylacetone and benzoyltrifluoroacetone
Figure 19. Phosphorescence Spectra of Irradiated Dibenzoylmethane

a. Blue and Green Phosphorescence in 3-methylpentane

b. Blue Phosphorescence in EPA

c. Green Phosphorescence in EPA
in 3-methylpentane are shown in Figure 20 and Figure 21, respectively. Both give the blue and the green phosphorescences. The original benzoylacetone in 3-methylpentane has a stronger green phosphorescence with vibrational bands at 510 μm (19610 cm\(^{-1}\)) and 480 μm (20830 cm\(^{-1}\)) and a weaker blue phosphorescence with vibrational bands at 455 μm (21980 cm\(^{-1}\)), 422 μm (23700 cm\(^{-1}\)) and 395 μm (25320 cm\(^{-1}\)). After benzoylacetone in the 3-methylpentane glass was exposed to the full intensity of the A-H\(_6\) for 10 minutes, the intensity of the blue phosphorescence becomes stronger than that of the green phosphorescence. The relative intensity and the positions of the vibrational bands of each phosphorescence do not change upon irradiation. Benzoyl trifluoroacetone behaves in a manner similar to that of benzoylacetone. When the exciting light is turned on it gives a strong green phosphorescence with vibrational bands at 520 μm (19320 cm\(^{-1}\)) and 488 μm (20490 cm\(^{-1}\)), and a weak blue phosphorescence with vibrational bands at 445 μm (22470 cm\(^{-1}\)), 420 μm (23810 cm\(^{-1}\)) and 395 μm (25320 cm\(^{-1}\)). The intensity of the blue phosphorescence increases with the time of excitation, while the intensity of the green phosphorescence remains almost constant. In 3-methylpentane irradiated 2-bromo-1,3-diphenyl-1,3-propanedione gives a green and a blue phosphorescences.

In order to understand the origin of the different phosphorescences in more detail, the phosphorescence excitation spectrum has been studied for each phosphorescence of every compound. The vibrational bands in each phosphorescence gave the same excitation
Figure 20. Phosphorescence Spectra of Benzoylaceton in 3-Methylpentane

a. Before Irradiation

b. After Irradiation with the A-H6 for 10 mins.
Figure 21. Phosphorescence Spectra of Benzoyltrifluoroacetone in 3-Methylpentane

a. Initially

b. After 10 minutes of Irradiation with the Exciting Light

c. After 25 minutes of Irradiation with the Exciting Light
spectrum. All blue phosphorescence excitation spectra show two peaks which are very close to each other at the region of 240 - 280 nm. These correspond to the absorption bands of the intermediate wavelength. The weak band of long wavelength in the phosphorescence excitation spectra cannot be found in the absorption spectra. It is believed that this band is hidden under the strong intramolecular charge transfer band in the absorption spectra. The blue phosphorescence excitation spectra of benzoylacetone, benzoyltrifluoroacetone, dibenzoylmethane and benzaldehyde in EPA are shown in Figure 22. The green phosphorescence excitation spectra are shown in Figure 23; they are identical with the absorption spectra of the original molecules. The comparison of a part of the green phosphorescence excitation spectrum and the intramolecular charge transfer band of dibenzoylmethane in EPA at 77°K is shown in Figure 24. From the similarity between the phosphorescence excitation spectra and the absorption spectra of the original molecule, the fact that the green phosphorescence appears as soon as the exciting light is on, and the fact that only green phosphorescence is observed with the exciting light in the region of the intramolecular charge transfer band, it is believed that the green phosphorescence comes from the original molecule, which mainly consists of the chelated enol form. It is proposed that the blue phosphorescence comes from the keto form of β-diketones. This conclusion has the following bases. (1) The blue phosphorescence is strong compared with the green phosphorescence in EPA, while it is
Figure 22. Excitation Spectra of Blue Phosphorescence in EPA

a. Benzoylacetone
b. Benzoyltrimfluoroacetone
c. Dibenzoylmethane
d. Benzaldehyde
Figure 23. Excitation Spectra of the Green Phosphorescence in EPA

a. Dibenzocymethane \((\text{C}_6\text{H}_5\text{C(OH):CHCOC}_6\text{H}_5)\)

b. Benzoylacetonate \((\text{C}_6\text{H}_5\text{C(OH):CHCOCH}_3)\)

c. Benzoyltrifluoroacetone \((\text{C}_6\text{H}_5\text{C(OH):CHCOCF}_3)\)
Figure 24.  

a. Absorption Spectrum of Dibenzoylmethane in EPA at 77°K  
b. Green Phosphorescence Excitation Spectrum of Dibenzoylmethane in EPA at 77°K
very weak in hydrocarbon and its intensity builds up in the latter solvent. The keto-enol tautomeric equilibrium can be considered to be an acid-base equilibrium of two acids - the keto form, a stronger acid, and the chelated enol form, a weaker acid. In hydrocarbon, a non-polar solvent, the equilibrium should displace to the chelated enol form: it is solvated more readily in the non-polar solvent. In EPA, which is a polar solvent, the equilibrium should be displaced toward the keto form, which is more readily solvated in the polar solvent. β-Diketones exist mainly in the chelated enol form. There are some keto forms in EPA. Irradiation with the UV light will convert the chelated enol into the less stable keto form. The conversion causes the increase in intensity of the blue phosphorescences of β-diketones in the hydrocarbon solvent. The larger shift of the blue phosphorescence than of the green phosphorescence of dibenzoylmethane as solvents vary from hydrocarbon to EPA also supports this mechanism. The chelated enol form, which causes the green phosphorescence, should be less affected by the solvent because of the presence of the intramolecular hydrogen bond in the molecule. The keto form, which gives the blue phosphorescence, should be affected more as the solvent changes from hydrocarbon to a polar solvent, EPA. (2) Consider the half life of the blue phosphorescences, their values are in the order of $10^{-2}$ sec. which is a reasonable magnitude for a $(n, \pi^*)$ phosphorescence. It is thought that all the keto forms of β-diketones have a lowest $(n, \pi^*)$ excited singlet state. This argument can be
supported further by considering the vibrational frequencies of the blue phosphorescence. The $C=O$ stretching band in the ground state, which has a value around $1650 \text{ cm}^{-1}$, can be observed in the blue phosphorescences. This indicates that the blue phosphorescence involves an excitation of a non-bonding electron on the carbonyl group. The similarities between the blue phosphorescences of a $\beta$-diketones and the phosphorescence of benzaldehyde and between their phosphorescence excitation spectra leads one to believe that the blue phosphorescences are from a slightly perturbed benzaldehyde molecule. This confirms our assignment that the blue phosphorescences come from the keto tautomer of $\beta$-diketones. The fact that no blue phosphorescence is observed when the exciting light is in the region of the intramolecular charge transfer band indicates that the blue phosphorescence does not come from the unchelated enol form. The unchelated enol form still has the intramolecular charge transfer band, which is slightly displaced to the short wavelength side in comparison with the intramolecular charge transfer band of the chelated enol. The buildup of the blue phosphorescence also excludes the possibility that the blue phosphorescence comes from the unchelated enol. The intramolecular hydrogen bond should be broken as soon as the UV excitation occurs. The conversion of the enol form into the keto form involves a migration of a hydrogen atom, which is a diffusion-controlled pro-

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cess. That causes the intensity of the blue phosphorescence in the hydrocarbon solvent to increase gradually. The presence of the blue phosphorescence and the absence of the green phosphorescence in 2-bromo-1,3-diphenyl-1,3-propanedione support our mechanism. This compound exists mainly in the keto form which gives only the blue phosphorescence. The presence of the green phosphorescence and the blue phosphorescence from the irradiated 2-bromo-1,3-diphenyl-1,3-propanedione in 3-methylpentane also verifies the assignments.

Of all the β-diketones studied at 77°K only dibenzoylmethane has a fluoresce. Dibenzoylmethane has a strong blue fluorescence in either hydrocarbon or EPA. The fluorescence spectrum is not affected by the presence of oxygen. The degassed sample and the sample without degassing gave the same fluorescence. In IPMP the fluorescence spectrum of dibenzoylmethane has four peaks at 445 μm (22470 cm⁻¹), 433 μm (23090 cm⁻¹), 420 μm (23810 cm⁻¹) and 400 μm (25000 cm⁻¹) as shown in Figure 25. The observed vibrational frequencies of the ground state of dibenzoylmethane in IPMP are 620 cm⁻¹, 720 cm⁻¹ and 1190 cm⁻¹. The spectra were taken with exciting light at wavelengths of 379 μm, 361 μm, 350 μm, and 250 μm. The positions and relative intensity of the fluorescence maxima do not change by varying the wavelength of the exciting light. This indicates that the fluorescence comes from the lowest excited singlet state of the molecule. The intensity of the fluorescence spectra decreases as the exciting wavelength decreases. This is caused by the
Figure 25. Fluorescence and Absorption Spectra of Dibenzoylmethane at 77°K

a. Absorption Spectrum in IPMP
b. Fluorescence Spectrum in IPMP
c. Absorption Spectrum in EPA
d. Fluorescence Spectrum in EPA
fact that the output intensity of the Cary 15 monochromator decreases as the wavelength decreases. No green or blue phosphorescence has been observed in the total emission spectrum. The intensity of the exciting light through the monochromator is too weak to have observed the phosphorescence spectrum in the total emission spectrum. The exciting wavelengths utilized in obtaining the fluorescence spectra of dibenzoylmethane in EPA are 378 μm, 359 μm, 344 μm, and 250 μm. They all gave identical fluorescences with different total intensities but identical relative band intensities. The fluorescence spectrum of dibenzoylmethane in EPA has four peaks at 445 μm (22470 cm⁻¹), 420 μm (23810 cm⁻¹), 400 μm (25000 cm⁻¹) and 386 μm (25910 cm⁻¹). The observed vibrational frequencies are 1340 cm⁻¹, 1190 cm⁻¹ and 910 cm⁻¹. No 1650 cm⁻¹ vibrational frequency, which corresponds to the stretching of the C=O group has been observed in the fluorescence spectra. The fluorescence spectra of dibenzoylmethane in IPMP and EPA are shown in Figure 25 with the intramolecular charge transfer band of the molecule in IPMP and EPA at 77°K. The absorption spectrum and its corresponding fluorescence have approximate mirror-image relationship. This indicates that the geometries of the ground state and of the first excited singlet state are similar. Since the intramolecular hydrogen bond exists in the ground state of dibenzoylmethane it would be expected that it exists in the first excited singlet state also.

Normally an aromatic compound with a lowest excited singlet
state which is \((n, \pi^*)\) does not fluoresce. A comparison between the absorption spectra of the chelated \(\beta\)-diketones and their corresponding green phosphorescences leads to the conclusion that the lowest excited singlet state of the chelated \(\beta\)-diketones is a \((\pi, \pi^*)\) state rather than an \((n, \pi^*)\) state. If one considers the 0-0 band of the intramolecular charge transfer band of the chelated dibenzoylmethane in EPA at 77\(^\circ\)K, which is at 378 \(\text{nm}\) (264.50 \(\text{cm}^{-1}\)) and the 0-0 band of the green phosphorescence of dibenzoylmethane in EPA, which is at 490 \(\text{nm}\) (20410 \(\text{cm}^{-1}\)), he finds that the singlet-triplet separation is 6040 \(\text{cm}^{-1}\). The similar singlet-triplet separations of the chelated benzoylaceton and benzoyl trifluoracetone in EPA are 7070 \(\text{cm}^{-1}\) and 5990 \(\text{cm}^{-1}\), respectively. These values are too large for an \((n, \pi^*)\) singlet-triplet separation. Therefore the lowest excited singlet state of the chelated enol form of \(\beta\)-diketones is a \((\pi, \pi^*)\) state. This assignment may be supported by the fact that the green phosphorescence is weaker relative to the blue phosphorescence, which is an \((n, \pi^*)\) phosphorescence. In the keto form the electronic structures of benzoylaceton, benzoyl trifluoracetone and dibenzoylmethane are similar to those of benzaldehyde but they are slightly perturbed by the substituents. There exists a great similarity between both the blue phosphorescences and the excitation spectra of these compounds. On the basis of data for the singlet-triplet separations of a group of aromatic ketones (1765 \(\text{cm}^{-1}\) for benzaldehyde, 1820 \(\text{cm}^{-1}\) for acetophenone and 2135 \(\text{cm}^{-1}\) for
benzophenone), it seems reasonable to assume that the separation of the singlet–triplet levels of the \((n, \pi^*)\) states of benzoylacetone, benzoyltrifluoroacetone and dibenzoylmethane is approximately \(2000 \text{ cm}^{-1}\). The approximate positions of the \((n, \pi^*)\) singlet states can be obtained by adding the singlet–triplet separation to the 0–0 band of the blue phosphorescence of the appropriate molecules. The calculation suggests that the \(n \rightarrow \pi^*\) transitions should occur around 360 \(\text{mu}\) for benzoylacetone, 370 \(\text{mu}\) for benzoyltrifluoroacetone and 350 \(\text{mu}\) for dibenzoylmethane; it does occur at 371 \(\text{mu}\) in the case of benzaldehyde. The first \(\pi \rightarrow \pi^*\) transitions of these compounds are near 280 \(\text{mu}\) and are observed in the blue phosphorescence excitation spectra. Therefore, the lowest excited singlet states of \(\beta\)-diketones in the keto form are \((n, \pi^*)\) states. There is no data available with which to estimate the approximate positions of the \((n, \pi^*)\) states of \(\beta\)-diketones in the unchelated enol form. But it can be safely assumed that the \(n \rightarrow \pi^*\) transitions of these molecules are at lower energies than the \(n \rightarrow \pi^*\) transition of benzaldehyde, which is at 371 \(\text{mu}\). This assignment is based on the fact that in benzoylacetone, benzoyltrifluoroacetone and dibenzoylmethane the \(C = O\) group is connected to both a phenyl ring and a vinyl group, while in benzaldehyde the \(C = O\) group is connected to a phenyl ring only. The 0–0 band of the intramolecular

charge transfer band of β-diketones in the unchelated enol form is at wavelengths smaller than 375 nm. It is reasonable to assume that the lowest excited singlet state of β-diketones in the unchelated enol form is an \((n, \pi^*)\) state. In the chelated enol form of β-diketones the situation is different. By formation of the intramolecular hydrogen bond in the chelated enol form, the non-bonding character of the electron on the oxygen atom is lost almost completely or to some extent and the level of \((n, \pi^*)\) singlet state is raised remarkably. The formation of the intramolecular hydrogen bond lowers the the level of the first \((\pi, \pi^*)\) singlet state also. This is indicated in the red-shift of the intramolecular charge transfer band upon the formation of the intramolecular hydrogen bond. For this reason the first excited singlet state of β-diketones in the chelated enol form is a \((\pi, \pi^*)\) state.

The lack of observable fluorescence in benzoylacetone and benzoyltrifluoroacetone can be explained that in these two molecules the radiationless transitions compete more effectively and no fluorescence can be observed. A possible interpretation, which has been applied by El-Sayed to nitrogen heterocyclics\(^{43}\), is given. In benzoylacetone and benzoyltrifluoroacetone the energy level of the \((n, \pi^*)\) singlet state is higher than that of the first \((\pi, \pi^*)\) singlet state, and the energy level of the \((n, \pi^*)\) triplet state is

higher than that of the first ($\pi, \pi^*$) triplet state. It is probable that the ($\pi, \pi^*$) singlet state is higher than the ($n, \pi^*$) triplet state. If this is the case the efficient intersystem crossing between the first ($\pi, \pi^*$) singlet state and the ($n, \pi^*$) triplet state occurs and no fluorescence can be observed. In dibenzoylmethane, the energy level of the ($n, \pi^*$) singlet state is higher than that of the first ($\pi, \pi^*$) singlet state, and the ($n, \pi^*$) triplet state is higher than the first ($\pi, \pi^*$) triplet state. It is possible that the first ($\pi, \pi^*$) singlet excited state has a lower energy value than the ($n, \pi^*$) triplet level. This would lead to a retardation of the intersystem crossing process and allow the fluorescence to be observed.

A possible mechanism of the photochemical process of $\beta$-diketones in the rigid glass is proposed and summarized in Figure 26. In this figure the energy levels with solid line are obtained from the experiments, the energy levels with the dotted line are hypothetical and have not been obtained from experiment. The absorption and radiative transitions between energy levels are expressed with solid lines and the radiationless transitions are represented by the broken lines.

$\beta$-Diketones can exist as the chelated enol form, the keto form, and the unchelated enol form. The chelated enol form is the most stable one, the unchelated enol is the least stable one and the keto form has an intermediate stability. This assignment will be
Figure 26. Photochemical Processes of the β-Diketones in the Rigid Glasses

S, Singlet State; T, Triplet State;
Subscripts CE, UC, K Represent the Chelated Enol, Unchelated Enol and Keto, Respectively;
Subscripts 0, 1, 2, 3 Represent the Ground State, first the Excited State, 2nd Excited State and 3rd Excited State, Respectively.
justified by the nuclear magnetic resonance study in Chapter 2. In
hydrocarbon solvent β-diketones exist almost exclusively in the
chelated enol form. This form is stabilized by the formation of an
intramolecular hydrogen bond. The lower the temperature is, the
stronger is the intramolecular hydrogen bond. This causes the red-
shift of the intramolecular charge transfer band as the temperature
decreases from the room temperature to the liquid nitrogen tempera-
ture. Upon irradiation, the chelated enol form will be excited from
the ground state, $S_{0CE}$ to the first excited singlet state, $S_{1CE}$, the
second excited singlet state, $S_{2CE}$, etc. The higher excited singlet
states lose their energy through radiationless transitions to the
first excited singlet state. The degradation of $S_{1CE}$ can be through
the fluorescence to the ground state or through the intersystem
crossing to the excited triplet state of the chelated enol, $T_{1CE}$,
from which the green phosphorescence is emitted. The $T_{1CE}$ state can
be degraded through the radiationless transition also. $S_{1CE}$ can
lose energy by transferring it to the ground state of the unchelated
enol, $S_{0UC}$. It is believed that the lowest excited singlet state of
the unchelated enol to be an $(n, \pi^*)$ state, which is not observable
in these experiments. The only observable transition in the un-
chelated enol is the $S_{0UC} \rightarrow S_{2UC}$, which corresponds to the intramo-
lecular charge transfer band in the chelated enol form. The sep-
aration of these two states is larger than the separation of $S_{0CE}$
and $S_{1CE}$. This means that the intramolecular hydrogen bond stabi-
lize the first excited singlet state more than the ground state of
$\beta$-diketones. Internal conversion between $S_{2UC}$ and $S_{1UC}$ takes place very fast. Since $S_{1UC}$ is an $(n, \pi^*)$ state, intersystem crossing to $T_{1UC}$ is very probable. $T_{1UC}$ is the intermediate state from which the energy transfer between the enol form and the keto form takes place. Non-radiative transition from $T_{1UC}$ to $S_{0UC}$ is also possible. Because of these two competitive processes no phosphorescence from $T_{1UC}$ has been observed. $S_{0K}$, which is the ground state of the keto form, can be excited into different excited states. The transition between the ground state of the keto form, $S_{0K}$, and its first excited singlet state, $S_{1K}$, which is an $(n, \pi^*)$ state, has not been observed. The $S_{0K} \rightarrow S_{2K}$ and $S_{0K} \rightarrow S_{3K}$ transitions can be obtained from the blue phosphorescence excitation spectra. Internal conversions between $S_{3K} \rightarrow S_{2K}$, $S_{2K} \rightarrow S_{1K}$, and $S_{3K} \rightarrow S_{1K}$ take place. Intersystem crossing between $S_{1K}$ and $T_{1K}$ occurs relatively easily. Blue phosphorescence is observed from the $T_{1K}$ state. The process of $T_{1UC} \rightarrow S_{0K}$ is the diffusion controlled process which involves the migration of a hydrogen atom. In EPA glass there are some molecules in the keto form. It is not necessary to have $T_{1UC} \rightarrow S_{0K}$ in order to obtain the blue phosphorescence. That is the reason that $\beta$-diketones in EPA emit the blue phosphorescences as soon as the molecule receives the initial excitation. The separation of the energy levels are given in Table 4. In Table 4 $S_{0CE} \rightarrow S_{1CE}$'s are obtained from the 0-0 bands of the intramolecular charge transfer band of $\beta$-diketones in IPMP (H.C.) and EPA at 77°K, $S_{0CE} \rightarrow S_{2CE}$ and $S_{0CE} \rightarrow S_{3CE}$ are obtained from
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the absorption spectra at room temperature in cyclohexane (H.C.) and isopropyl alcohol (alc.). $S_{OCE-T_{ICE}}$ is the 0-0 band of the green phosphorescence and $S_{OK-T_{IK}}$ is the 0-0 band of the blue phosphorescence. $S_{OUC-S_{2UC}}$ is obtained from the 0-0 band of the intramolecular charge transfer band of the irradiated molecules, which has been irradiated with the A-H6 for 60 minutes at 77°K. $S_{OK-S_{2K}}$ and $S_{OK-S_{3K}}$ are obtained from the blue phosphorescence excitation spectra. $S_{OCE-S_{OK}}$'s are the $4H^0$'s of the keto-enol tautomeric reaction, which are obtained from the nuclear magnetic resonance experiments.
IV. SUMMARY

By means of electronic spectroscopic studies photochemical reactions of β-diketones at 77°K have been observed. These photochemical reactions are believed to be the results of keto-enol tautomeric equilibria which have unchelated enols as intermediates. β-Diketones exist mainly in the chelated enol form in the hydrocarbon solvent especially at 77°K. The less stable forms, the keto form and the unchelated enol form, can be generated by irradiation of the chelated enol form. Some keto form exists in EPA. All chelated enols give green phosphorescences. Fluorescence is observed in the chelated enols only in the case of dibenzoylmethane. This has been interpreted to indicate that in the chelated enol of dibenzoylmethane the energy level of $T_2(n, \pi^*)$ state is higher than the $S_1(\pi, \pi^*)$ state. No phosphorescences or fluorescences are observed from the unchelated enols which have $(n, \pi^*)$ lowest singlet states. The absence of the phosphorescence is explained by energy transfer from the $T_{1UC}$ state to the ground state of the keto form and a non-radiative transition from its $T_{1UC}$ state to its $S_{0UC}$ state which occurs more readily than does the radiative transition. The keto form gives a strong blue phosphorescence and no fluorescence. A detailed mechanism of the photochemical processes, which can interpret the observed phenomena qualitatively, has been proposed. Further justification of this mechanism has to be done.
Some experiments which may help to justify the mechanism are suggested. A detailed kinetic study to determine the absolute or the relative reaction rate constants of each process is necessary. It is a quite complicated problem. It can be approached through the quantum yield studies of the green phosphorescence, the blue phosphorescence and the fluorescence. These experiments should be carried out in the different concentrations with respect to the chelated enol form. The rate of decrease of the enol form, which is directly proportional to the rate of the decrease in the intensity of the intramolecular charge transfer band of the enol form, should be measured. Electronic spin resonance studies of the irradiated \( \beta \)-diketones in the rigid glass should be carried out to identify the metastable excited triplet states of each species. The assumption that no free radicals occur as intermediates can be verified by the E.S.R. studies. Flash photolysis experiments should be carried out. The observable triplet-triplet transition of the chelated enol form can further verify that the lowest excited triplet state of the chelated enol is a \( (\pi, \pi^*) \) state. This triplet-triplet absorption study can determine the concentration of the triplet as a function of time. Phosphorescence polarization measurements should be carried out on the blue and the green phosphorescence. If the assignments are correct the blue phosphorescence, which comes from the \( (n, \pi^*) \) triplet state, should be polarized in the molecular plane and the green phosphorescence, which comes from the \( (\pi, \pi^*) \) triplet state, should be polarized
perpendicular to the molecular plane.

The main problem left to be solved is to locate the \((n, \pi^*)\) state of each species. This cannot be done experimentally. Because the weak \(n \rightarrow \pi^*\) transition is hidden under the strong \(\pi \rightarrow \pi^*\) transitions and it is not observable. A semiempirical method of resonance can be applied to calculate the \(n \rightarrow \pi^*\) transitions and the transition of the longest wavelength band of \(\beta\)-diketones.

\(^4^4\) McGlynn, S. P., Seminar on Computational Methods, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana (1966).
NUCLEAR MAGNETIC RESONANCE STUDIES OF THE
ENOL-KETO TAUTOMERISM IN β-DIKETONES

I. Introduction

Nuclear magnetic resonance studies of β-diketones have been carried out by several authors. Reeves\(^1\) has studied the keto-enol tautomerism of pure liquid acetylacetone, and he has assigned all the chemical shifts in the spectrum. From the equilibrium constants of the keto-enol tautomerism at different temperatures he has estimated the enthalpy change of the keto-enol conversion. Hay and Williams\(^2\) have studied the hydroxyl proton shifts of acetylacetone, dibenzoyl-methane and benzoylacetone at room temperature and have determined the enol composition of each compound. These compounds have been studied by Burdett and Rogers at room temperature and various other temperatures. They have calculated the thermodynamic quantities for the keto-enol tautomerism of acetylacetone and its derivatives.\(^3,4\)

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\(^1\) Reeves, L. W., Can. J. Chem. 35 1351 (1957).


\(^3\) Burdett, J. L. and M. T. Rogers, J. Am. Chem. Soc. 86 2105 (1964).

The proton with a spin of $\frac{1}{2}$ has a magnetic moment of magnitude

$$\mu = g \mu_N \sqrt{\frac{1}{2} \left( \frac{1}{2} + 1 \right)} = \frac{\sqrt{3}}{2} \ g \mu_N$$  \hspace{1cm} (1)$$

The quantity $\mu_N$ is the nuclear magneton and $g$ is the $g$-factor of the proton. When the proton is placed in a magnetic field $\hat{H}_0$, the energy of the proton in the field, is given by the equation

$$W = \mu \cdot \hat{H}_0 = \mu H_0 \cos \theta$$  \hspace{1cm} (2)$$
in which $\theta$ is the angle between $\mu$ and $\hat{H}_0$. $W$ can assume two values; i.e., there are two orientations of proton spin with respect to the applied field. Each nuclear moment has two components, one of magnitude $\pm \frac{g \mu_N}{2}$ parallel to the field, and the other of magnitude $\frac{g \mu_N}{2}$ perpendicular to the field. The $\pm$ sign in front of the parallel components denotes the two possible nuclear magnetic energy levels, one in which the component is parallel and the other in which it is antiparallel to the field, the latter having the higher energy. The actual moment, of a magnitude given by equation (1), is inclined at an angle to $\hat{H}_0$ and precesses around the field vector. As a result of this magnetic quantization, when a molecule containing a hydrogen atom is placed in a magnetic field, apart from rotational and vibrational transitions which occur in the ground electronic state, there is also the possibility of magnetic transitions between the two nuclear magnetic energy levels defined by their antiparallel components $+ \frac{g \mu_N}{2}$ and $- \frac{g \mu_N}{2}$. The Bohr frequency condition states that this difference in energy between the two levels is equivalent to
frequency \( \nu \) given by

\[ h\nu = g_{\mu N} H_0 \]  (3)

The precession of \( \hat{\mu} \) around \( \hat{H}_0 \) will itself give rise to a magnetic field, which may be resolved into two components, a static component \( H_z \) along \( \hat{H}_0 \) and a rotating component perpendicular to \( \hat{H}_0 \). The precessional movement of the nuclear magnetic about the applied field is familiar from Larmor's classical theorem; any magnet of moment \( \mu \) in a field \( \hat{H}_0 \) will precess around the direction of the field with an angular velocity given by

\[ h\omega = 2\pi g_{\mu N} H_0 \]  (4)

The frequency of the rotating field produced by this precessing magnet at right angles to \( \hat{H}_0 \) is \( \omega/2\pi \). If there is superimposed on this system perpendicular to \( \hat{H}_0 \) an oscillatory magnetic field, \( \hat{H}_1 \), of the same periodicity, the precessing nucleus and the oscillatory field can exchange energy and the nuclear magnet can be made to 'flop' between the parallel and the antiparallel states. This system of a static field \( \hat{H}_0 \) and an oscillatory field \( \hat{H}_1 \), applied perpendicular to \( \hat{H}_0 \), produces the essential conditions for the nuclear magnetic resonance experiment.

From what has been said so far, it might be supposed that at any particular radio frequency \( \nu \), all proton nuclei would resonate at the same value of \( H_0 \). Actually, resonance occurs at different values of \( H_0 \) for each type of proton. The effective magnetic field which is measured in the resonance experiment is
\[ H = H_0 (1 - \sigma) \]

in which \( \sigma \), which is usually referred to as the screening constant, is a dimensionless constant independent of \( H_0 \) but dependent on the chemical (electronic) environment. The screening field \( (-\sigma H_0) \) is the secondary magnetic field due to the electronic currents induced by the primary field \( H_0 \). If we measure the proton magnetic resonance spectra of the hydrogen atom in various chemical environments, either in different molecules or in different chemical positions in the same molecule, there will be a corresponding set of different values of the screening constants. As a result, resonance will occur in a different part of the spectrum for each chemically distinct position. This displacement of a signal for different chemical environments due to variations in screening constants is referred to as a chemical shift.

Factors which contribute to the proton magnetic screening constant can be attributed both to chemical terms, which originated from the different chemical environments, and to physical terms resulting from the influence of the surrounding medium. The chemical contribution has been divided for singlet state molecules into subterms such as

\[ \sigma_c = \sigma_d + \sigma_p + \sigma_a + \sigma_e \]

The Lamb diamagnetic contribution, \( \sigma_d \), results from the uniform

\(^{5}\text{Grant, D. M., Annual Review of Physical Chemistry, 15, 489 (1964).}\)
circulation of atomic electrons in a magnetic field. To correct for
the effect of molecular environment upon this free flow of electrons,
a localized paramagnetic term, $\sigma_p$, is introduced. This paramagnetic
perturbation of an atom results from an admixture by the applied
magnetic field of electronic states into the ground state wave func-
tion. The third term $\sigma_a$ represents the magnetic screening due to
anisotropic groups which may be present in a molecule. Typical of
such groups are aromatic ring systems and magnetically anisotropic
chemical bonds in which the difference between the perpendicular and
parallel magnetic susceptibilities are significant. The reaction
field effect, $\sigma_r$, results from intramolecular electrical dipole-dipole
interaction or contributions from interatomic current.

Chemical shifts due to the influence of the surrounding medium
are related to the physical interactions by

$$\sigma' = \sigma_b' + \sigma_w' + \sigma_r' + \sigma_n'$$

The bulk diamagnetic susceptibility influence is denoted by $\sigma_b'$. 
Dispersion forces of the van der Waals type create magnetic field
shifts represented by $\sigma_w'$, and the intramolecular reaction field term
is given by $\sigma_r'$. Magnetic anisotropic shifts have been observed be-
tween neighboring molecules and those terms are represented by $\sigma_n'$. 

It is well documented that hydrogen bond formation causes the
proton magnetic resonance signal of the involved proton to shift to
lower fields. The principal contributions to this shift were suggest-
ed some time ago and are easily summarized. (1) A contribution to
the proton screening (always negative) due to the distortion of the electronic structure of the chemical bond in which the proton is involved. (2) A contribution (negative or positive) to the proton screening due to any magnetic anisotropy of the molecule to which the proton is hydrogen-bonded.

For a given kind of nucleus, the area under the resonance curve is expected to be closely proportional to the number of nuclei per unit volume, or the concentration of the nuclei involved. Actually, the area under the absorption signal is

\[ A_a \propto \frac{X_0 H_1}{(1 + \gamma^2 H_1^2 T_1^{-1} T_2)^{1/2}} \]

in which \( H_1 \) is the oscillatory field, \( \gamma \) is magnetogyric ratio, \( T_1 \) and \( T_2 \) are the spin-lattice relaxation time and the spin-spin relaxation time, respectively, and \( X_0 \) is the magnetic susceptibility which is directly proportional to the number of nuclei per unit volume.

The present study has involved two aliphatic \( \beta \)-diketones, acetylacetone and hexafluoroacetylacetone, and two aromatic \( \beta \)-diketones, benzoylacetonate and dibenzoylmethane. The keto-enol tautomeric equilibrium which is considered in this study is:

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The enol tautomers exist mainly in conjugate chelate forms through the formation of the intramolecular hydrogen bond. Temperature effects on the intramolecular hydrogen bond are considered. The equilibrium constants and the thermodynamic quantities for the tautomerism at different temperatures are given.
II. EXPERIMENTAL

The sources of acetylacetone, hexafluoroacetylacetone, benzoylacetone and dibenzoylmethane and their procedures of purification were given in the experimental part of Chapter 1.

Proton magnetic resonance spectra were obtained with a Varian HA-60 spectrometer, V-4340 variable temperature probe accessory and V-4331-THR spinning sample dewar probe insert. Samples were sealed in a 5 mm O.D. cylindrical glass tube. Tetramethylsilane was used as an internal reference. Before they were sealed, the sample and the internal reference were degassed by subjecting them to repeated cycles of freezing, pumping and thawing. In order to ensure thermal equilibrium, spectra were taken at least 30 minutes after the sample system reached the desired temperature. The temperature range studied was above the melting point of the compound and below the maximum temperature limit of the instrument. All compounds were studied in pure liquid states.

The concentrations of keto and enol tautomers were obtained by integrating the intensity of CH₂ and CH peaks in the keto and enol forms respectively. At least three integrations were performed, and the percentages of enol tautomer were accurate to within ± 2%. The radiofrequency power was kept well below saturation and above the threshold at which signal intensity becomes proportional to the proton concentration.

In order to rule out the possibility of thermal decomposition
of the sample, UV absorption spectra of each sample were taken before and after heating the sample. No changes in the spectra were observed.
Proton magnetic chemical shifts of acetylacetone, hexafluorooacetetylacetone, benzoylacetone and dibenzoylmethane are given in Table 1 in c.p.s. units with respect to the internal reference tetramethylsilane at 60 MC. Of all the protons in these compounds the CH₃ protons in acetylacetone and benzoylacetone resonate at the highest magnetic fields. Their signals appear around 120 c.p.s. for CH₃ in the enol tautomer and 130 c.p.s. for CH₃ in the keto tautomer. Their assignments are based upon the relative magnitude of the intensity of the peaks and the temperature effects on the intensity of the peak. Since both acetylacetone and benzoylacetone are more stable in the enol tautomer, the intensity of the CH₃ peak in enol tautomer should be larger than the intensity of the CH₃ peak in keto tautomer.

The 120 c.p.s. peak is larger than the peak of 130 c.p.s. The peak around 130 c.p.s. increases with increase in temperature, while the 120 c.p.s. decreases as temperature increases. On increasing the temperature the tautomerism shifts to the keto side and increases the keto content. In the case of either the keto form or enol form the resonance position of CH₃ proton does not shift too much in going from acetylacetone to benzoylacetone. The methyl group in acetylacetone and the phenyl group in benzoylacetone are too remote from the acetyl methyl proton to cause a substantial difference in the position of the CH₃ resonance. The CH₃ shifts are essentially independent of temperature.
# TABLE 1

PROTON CHEMICAL SHIFTS IN PURE α-DIKETONES

<table>
<thead>
<tr>
<th>°C</th>
<th>CH(e)*</th>
<th>CH(e)*</th>
<th>CH₂(k)+</th>
<th>CH₃(k)+</th>
<th>CH₃(e)*</th>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>25</td>
<td>920</td>
<td>336</td>
<td>220</td>
<td>131</td>
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<td>40</td>
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<td>185</td>
<td>873</td>
<td>331</td>
<td>213</td>
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<td>118</td>
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Hexafluorocacetylacetone

<table>
<thead>
<tr>
<th>°C</th>
<th>CH(e)*</th>
<th>CH(e)*</th>
<th>CH₂(k)+</th>
<th>CH₃(k)+</th>
<th>CH₃(e)*</th>
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<td>175</td>
<td>772</td>
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Benzoylaceton

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<tr>
<th>°C</th>
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<th>CH(e)*</th>
<th>CH₂(k)+</th>
<th>CH₃(k)+</th>
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<td>955</td>
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<tr>
<td>190</td>
<td>949</td>
<td>365</td>
<td>237</td>
<td>128</td>
<td>122</td>
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Dibenzoylmethane

<table>
<thead>
<tr>
<th>°C</th>
<th>CH(e)*</th>
<th>CH(e)*</th>
<th>CH₂(k)+</th>
<th>CH₃(k)+</th>
<th>CH₃(e)*</th>
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<td>403</td>
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<td>117</td>
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<td>403</td>
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<tr>
<td>136</td>
<td>1013</td>
<td>405</td>
<td>268</td>
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</tbody>
</table>

* enol tautomer

† keto tautomer
The $\alpha$-proton of CH$_2$ in the keto tautomer of acetylacetone, benzoylaceton, hexafluoroacetylacetone and dibenzoylmethane resonates in the regions of 215 c.p.s., 238 c.p.s., 250 c.p.s. and 267 c.p.s., respectively. The corresponding $\alpha$-proton signals in the enol tautomer occur near 333 c.p.s., 365 c.p.s., 387 c.p.s. and 403 c.p.s., respectively. The deshielding effect on the $\alpha$-proton increases in the order of acetylacetone, benzoylaceton, hexafluoroacetylacetone and dibenzoylmethane. The phenyl ring in benzoylaceton deshields the $\alpha$-proton, which is two atoms away from the substitutent and shifts the resonance signal of $\alpha$-proton to a lower field than that of the corresponding signal in acetylacetone. The fluoro groups, which have a high electronegativity, withdraw electrons from the rest of the molecule and consequently decrease the electron density of the neighborhood of $\alpha$-proton. This inductive effect is greater than the phenyl ring current effect; consequently the $\alpha$-proton signal of hexafluoroacetylacetone appears at a lower field than does that of the $\alpha$-proton of benzoylaceton. There are two phenyl rings in dibenzoylmethane. The phenyl ring current effects will augment one other and have the greatest deshielding effect on $\alpha$-proton. Enolic $\alpha$-proton peaks appear at lower magnetic fields than do the peaks of the $\alpha$-protons in the keto form. This is understandable when the types of bond between carbon and proton in the enol tautomer and in the keto tautomer are compared. In the enol tautomer the $\alpha$-proton is bound to the carbon via
an overlap of proton s orbital and a sp\(^2\) hybrid orbital of the carbon. While in the keto tautomer the carbon will utilize one of its sp\(^3\) hybrid orbital to overlap with the proton s orbital. There is more s character in the carbon-proton bond in the enol tautomer than in the one in the keto-tautomer. The increase of s character decreases the neighboring anisotropic effect on the \(\alpha\)-proton and increases the deshielding effect on it. In addition, the intramolecular hydrogen bond effect and the resonance effect, namely, the interatomic current effect, will play roles in shifting the \(\alpha\)-proton of the enol form to a field lower than that of the \(\alpha\)-proton of the keto form. The resonance effects are more important in dibenzoylmethane and benzoylacetone because of the possible presence of the resonance structures shown below.

This effect decreases the electron density in the neighborhood of the \(\alpha\)-proton and decreases the diamagnetic shielding of \(\alpha\)-proton by its own electrons. The chemical shifts of the \(\alpha\)-proton in benzoylacetone and dibenzoylmethane are independent of temperature. In
acetylacetone and hexafluoroacetylacetone they shift to higher magnetic fields with increase in temperature. The shift which is caused by increasing temperature is more pronounced in the keto tautomer. When the temperature increases from 25°C to 185°C the \( \alpha \)-proton peak shifts from 220 c.p.s. to 213 c.p.s. in the case of the keto tautomer of acetylacetone and from 336 c.p.s. to 331 c.p.s. in the case of the enol tautomer. The shift is 7 c.p.s. in the keto tautomer and 5 c.p.s. in the enol tautomer. For hexafluoroacetylacetone there are shifts of 8 c.p.s. and 4 c.p.s. for the enolic \( \alpha \)-proton and keto \( \alpha \)-proton respectively as temperature increases from 29°C to 175°C. These shifts have been explained by the effects of the rupture of the intermolecular hydrogen bonds and long range shielding.\(^7\)

The chemical shifts of the ring protons in benzoylaceton and dibenzoylmethane are independent of temperature. Two groups of resonance signals appear in each compound indicating the presence of two different kinds of ring protons. In benzoylaceton the two groups resonate at ca. 469 c.p.s. and at ca. 441 c.p.s. There are spin-coupling splittings associated with each group of the resonance. The splittings associated with the ca. 469 c.p.s. group are at 475 c.p.s., 473 c.p.s., 469 c.p.s., 465 c.p.s. and 463 c.p.s. The coupling constants are 4 c.p.s. and 2 c.p.s. The splittings

\(^7\)Burdett, J. E. and M. T. Rogers, \textit{op. cit.}

The hydroxyl proton peak of acetylacetone in the enol tautomer shifts from 920 c.p.s. to 873 c.p.s. as the temperature increases from 25°C to 185°C. The shift is from 783 c.p.s. to 772 c.p.s. for hexafluoroacetylacetone as the temperature increases from 29°C to 175°C. In benzoylaceton it shifts from 979 c.p.s. to 949 c.p.s. with the increase of temperature from 56°C to 190°C. This shift is from 1020 c.p.s. to 1013 c.p.s. for dibenzoylmethane as the temperature increases from 92°C to 136°C. The shift of the hydroxyl proton to higher magnetic fields is directly proportional to the temperature. A plot of the shifts vs. temperature gives a straight line for each compound as shown in Figure 1. The breaking of the intramolecular hydrogen bonds contributes to this deshielding effect. The higher the temperature the more the intramolecular hydrogen bonds are broken. It is well known that the formation of hydrogen bonds shifts the resonance position of the proton, which is involved
Figure 1. Chemical Shift of OH Signal vs. Temperature
in the hydrogen bonding, to lower magnetic fields.

Gutowsky, et al. have observed the deshielding effects on hydroxyl proton in the derivatives of phenols and naphthols when an intramolecular hydrogen bond is formed. They have related these chemical shifts to the strengths of the intramolecular hydrogen bonds and have shown that they are linearly proportional to the bond multiplicity of the ring bonds between the carbon atoms holding the chelated substituents. Similar arguments can be applied to the β-diketones. On formation of the intramolecular hydrogen bond the molecule undergoes quantitative change due to polarization. The approaching non-bonding electrons of the O⁻¹ atom will repel those forming the covalent O-H bond. This causes the OH resonance to shift to a lower magnetic field. Similarly, the attraction of the non-bonding O⁻¹ electrons by the proton will be accompanied by a repulsion of the O⁻¹ nucleus which will weaken its hold on these electrons. The effective nuclear charge of the O⁻¹ atom with regard to its other electrons will increase, resulting in electron shifts toward O⁻¹. Since the effects of both the increased electron-repelling character of the hydrogen atom and the increased electron attracting power of the O⁻¹ (or O) atom that form part of a ring system will superimpose on and reinforce each other, the polarization will be transmitted along the whole molecular system as shown by the arrows.

Through an inductive effect, the resultant charge on the $O^1$ (or $O$) atom will decrease the electron density in the neighborhood of the hydroxyl proton and decrease the $OH$ proton diamagnetic shielding by its own electrons. This effect becomes more important as the contribution of the following resonance structure in the chelated enol tautomer increases.

![Resonance Structure](image)

This is the major factor which causes the deshielding effect on the hydroxyl proton which is involved in an intramolecular hydrogen bond. The contribution of the above resonance structure to the chelated enol tautomer decreases in the order of dibenzoylmethane, benzoylacetonate, acetylacetone, and hexafluoroacetylacetone.

The enol contents of β-diketones decrease with increase in temperature (see Table 2). There is a straight line relationship between per cent enol tautomer and temperature as shown in Figure 2. There is 83% enol tautomer of acetylacetone at 25°C. As temperature
### TABLE 2

PERCENTAGES OF ENOL TAUTOMERS, EQUILIBRIUM CONSTANTS $\Delta G^0, \Delta S^0$ OF THE KETO$\leftrightarrow$ENOL TAUTOMERISM

<table>
<thead>
<tr>
<th>°C</th>
<th>% Enol</th>
<th>K</th>
<th>$-\Delta G^0 \times 10^{-3}$ (cal/mole)</th>
<th>$-\Delta S^0$ (cal/mole-deg.)</th>
</tr>
</thead>
</table>

**Acetylacetone**

| 25 | 83     | 4.7 | 0.92 | 4.6 |
| 40 | 79     | 3.8 | 0.83 | 4.7 |
| 70 | 72     | 2.6 | 0.65 | 4.8 |
| 100| 68     | 1.7 | 0.51 | 4.8 |
| 154| 62     | 1.6 | 0.31 | 4.6 |
| 185| 55     | 1.2 | 0.16 | 4.6 |

**Hexafluoroacetylacetone**

| 29 | 99.5   | 204 | 3.2 | 1.6 |
| 90 | 98.7   | 77.0| 3.1 | 1.4 |
| 130| 97.8   | 44.5| 3.0 | 1.5 |
| 175| 96.9   | 27.4| 3.0 | 1.6 |

**Benzoylaceton**

| 56 | 95     | 18.9| 1.9 | 5.1 |
| 84 | 91     | 10.5| 1.7 | 5.4 |
| 109| 90     | 9.6 | 1.7 | 5.0 |
| 136| 85     | 5.6 | 1.4 | 5.4 |
| 161| 80     | 4.0 | 1.2 | 5.6 |
| 190| 79     | 3.8 | 1.2 | 5.1 |

**Dibenzoylmethane**

| 92 | 97.2   | 35.5| 2.6 | 3.9 |
| 117| 96.2   | 25.3| 2.5 | 3.9 |
| 136| 95.2   | 20.0| 2.4 | 3.8 |
| 160| 94.0   | 15.6| 2.4 | 3.8 |
Figure 2. Temperature vs. Enol Contents

a. Acetylacetone (\(\text{CH}_2\text{C(\text{OH})CHCOCH}_3\))

b. Benzoylaceton

c. Dibenzoylmethane

d. Hexafluoroacetylacetone
increases to 185°C the enol tautomer decreases to 55%. For hexafluoroacetylacetone the effect of temperature on the enol-content is not too great. The enol-content of hexafluoroacetylacetone decreased from 99.5% to 96.9% with increase of temperature from 29°C to 175°C. As the temperature increases from 50°C to 190°C, the enol percentage of benzoylacetone decreases from 95% to 79%. The effect of temperature on the enol-content of dibenzoylmethane is that the enol tautomer decreases from 97.2% to 94.0% as the temperature increases from 92°C to 160°C. Data from this study show that the enol tautomer is more stable at low temperatures. If the data are extrapolated, the temperatures that acetylacetone, benzoylacetone, hexafluoroacetylacetone and dibenzoylmethane become 100% liquid enol tautomer can be predicted to be -85°C, 15°C, 21°C, and 47°C, respectively. As the temperature increases the tautomerism will shift toward the keto tautomer and the keto-content in the tautomeric mixture increases.

The equilibrium constant of the keto-enol tautomeric equilibrium, K, is defined as

$$K = \frac{[enol]}{[keto]} = \frac{\text{integrated intensity of } CH}{\text{integrated intensity of } CH_2/2}$$

in which [enol] and [keto] indicate the concentration of pure liquid enol and pure liquid keto, respectively. The K values for acetylacetone, hexafluoroacetylacetone, benzoylacetone and dibenzoylmethane at different temperatures are given in Table 2. A plot of log K vs. \(1/T\) gives a straight line for each compound as shown in Figure 3.
Figure 3. Temperature Dependence of the Equilibrium Constants.
In the dibenzoylmethane case there are some points that do not lie on the straight line. These points were obtained from the first series of experiments. All the signals corresponding to these points had a tail on the high field side which indicates that the resolution of the instrument was poor. They were taken about 10 minutes after the system reached the measuring temperature. It is thought that the time was too short for the establishment of thermal equilibrium. These are the factors which probably caused inaccurate results.

By means of the van't Hoff equation

\[- \Delta H^0 = R \cdot \frac{\text{d} \ln K}{\text{d}(1/T)}\]

the change of standard enthalpy, \(\Delta H^0\), for keto-enol tautomerism can be calculated from the slope of the curve of the \(\log K\) vs. \(1/T\). Pure liquid enol tautomer and pure liquid keto tautomer are taken to be the standard states. \(\Delta H^0\) for acetylacetone, hexafluoroacetylacetone, benzoylacetteone and dibenzoylmethane are \(-2.3\) Kcal/mole, \(-3.7\) Kcal/mole, \(-3.6\) Kcal/mole and \(-4.0\) Kcal/mole respectively. Burdett and Rogers have obtained a value of \(-2840\pm 200\) cal/mole for \(\Delta H^0\) of acetylacetone.\(^9\) \(\Delta H^0\) of acetylacetone was \(-2705\pm 100\) cal/mole according to Reeves.\(^10\) Powling and Bernstein have determined \(\Delta H^0\) of acetylacetone to be \(-2.4\) Kcal/mole by use of an infrared analytical

\(^9\)Burdett, J. S. and M. T. Rogers, \textit{op. cit.}

\(^10\)Reeves, L. W., \textit{op. cit.}
ΔH° can be subdivided into ΔH° = ΔHₘ - ΔHₖ in which ΔHₘ is the change of enthalpy due to the conversion of keto tautomer to open enol tautomer which does not form intramolecular hydrogen bond and ΔHₖ is the intramolecular hydrogen bond energy. In the formation of an intramolecular hydrogen bond, an energy, which is equivalent to the intramolecular hydrogen bond energy, will be released from the molecule. Since the enol tautomers exist exclusively in the chelated form, ΔHₖ has to be taken into consideration. Normally, ΔHₖ will have a value higher than 5 Kcal/mole, that means ΔHₖ is greater than zero for all cases in this study. This indicates that the open enol tautomer which does not form intramolecular hydrogen bond is less stable than the keto tautomer thermodynamically. It is the formation of the six-member ring via the intramolecular hydrogen bond in the enol tautomer that causes the enol tautomer to be more stable than the keto tautomer.

Values of the change of standard free energy, ΔG°, and the change of standard entropy, ΔS° can be calculated from,

$$\Delta G^0 = -RT\ln k$$

$$\Delta H^0 = \Delta G^0 - T\Delta S^0$$

Their values at different temperatures are given in Table 2. Acetylacetone has a ΔG° value of ca. -0.6 Kcal/mole. The ΔG° for hexafluoroacetylacetone is around -3.1 Kcal/mole, which is the

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largest change among all the compounds in this study. Benzoylaceton and dibenzoylemethane have $\Delta G^\circ$'s of about -1.7 Kcal/mole and -2.5 Kcal/mole respectively. All the $\Delta G^\circ$'s are negative. Their absolute values decrease as temperature increases. Since the change of free energy is a measurement of the degree of spontaneity of the reaction one expects that pure enol tautomer is more stable than the pure keto tautomer and the stability of the enol tautomer decreases with increase in temperature.

$\Delta S^\circ$'s are in the neighborhoods of -4.7 cal/mole-deg., -1.5 cal/mole-deg., -5.4 cal/mole-deg. and -3.8 cal/mole-deg. for acetylacetone, hexafluoroacetylacetone, benzoylaceton and dibenzoylemethane respectively. There is no direct relationship between $\Delta S^\circ$ and temperature. The negative values of $\Delta S^\circ$ indicate that the degree of randomness is higher in the keto tautomers than in the enol tautomers. This can be explained in the following ways: (1) In keto tautomer the orbitals of $\alpha$-carbon are $sp^3$ hybrids. They form $\sigma$-bonds with the neighboring atoms. In enol tautomer the orbitals of $\alpha$-carbon are $sp^2$ hybrids. They form two $\sigma$ single bonds and one $\pi$ double bond with the neighboring atoms. The formation of a double bond between $\alpha$-carbon and its neighboring carbon atom in the enol tautomer decreases the rotational freedom about this bond, the molecule becomes more rigid and consequently decreases the $\Delta S^\circ$ value. (2) In the enol tautomer there is a six-membered ring formed through intramolecular hydrogen bonding. In order to form the chelated structure the
0' atom and the O-H group have to be very close to each other and all the six members in the ring have to be in a plane. This eliminates some of the configurations which are possible in the keto tautomer.

The change of $\Delta S^o$ in hexafluoroacetylacetone is small compared to the changes of $\Delta S^o$ in other three compounds. This may be due to the presence of high electronegative fluoro groups in the hexafluoroacetylacetone. Fluoro groups in a molecule will strongly repel each other. They have to stay away from each other as far as possible. No matter whether they are in the keto tautomer or in enol tautomer the $\text{CF}_3$ groups have to be trans to each other. This causes other configurations in the keto tautomer to be highly improbable and decreases its entropy.
Nuclear magnetic resonance spectra of pure \( \beta \)-diketones have been studied at different temperatures. The effect of the temperature on the keto-enol tautomeric equilibrium has been studied. The increase in temperature displaces the equilibrium to the keto side. From the melting point of the compound to the maximum temperature limit of the instrument, 190°C, the major component in the equilibrium is the chelated enol form. Equilibrium constants of the keto-enol tautomeric equilibria have been determined at different temperatures. The highest temperatures at which \( \beta \)-diketones exist as 100% enol have been predicted to be \(-85^\circ\text{C}, 15^\circ\text{C}, 21^\circ\text{C}\) and \(47^\circ\text{C}\) for acetylacetone, benzoylacetone, hexafluoroacetylacetone and dibenzoylmethane, respectively. The change of the standard enthalpies of the keto-enol tautomerism have been calculated to be \(-2.3\text{ Kcal/mole}, -3.7\text{ Kcal/mole}, -3.6\text{ Kcal/mole}\) and \(-4.0\text{ Kcal/mole}\) for acetylacetone, hexafluoroacetylacetone, benzoylacetone and dibenzoylmethane, respectively. Other thermodynamic quantities have been obtained at different temperatures. Their values depend on the different molecular structures.
SELECTED BIBLIOGRAPHY


Nagakura, S., "Intramolecular Charge Transfer Spectra Observed with Some Compounds Containing the Nitro or the Carbonyl Group," The Journal of Chemical Physics, 23, 1441 (1955).


Jang Kuo was born in Shanghai, the Republic of China on August 15, 1936. He attended public schools in different cities in China. He graduated from the High School of Taiwan Normal University, Taipei, Formosa in 1954. He attended National Taiwan University, Taipei, Formosa from 1954 to 1958, when he received the degree of Bachelor of Science in Chemical Engineering. He was called to active duty in the Chinese army from 1958 to 1960.

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EXAMINATION AND THESIS REPORT

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Major Field: Chemistry

Title of Thesis: UV Spectroscopic and Nuclear Magnetic Resonance Studies of the Enol-Keto Tautomerism in \( \beta \)-Diketones.

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July 14, 1966