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The Kinetics and Mechanism of the Alkaline Fading of Iodo Phenol Blue - The Diacetone-Alcohol - Hydroxide Ion Reaction.

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THE KINETICS AND MECHANISM OF THE ALKALINE FADING OF IODO PHENOL BLUE. 
THE DIACETONE ALCOHOL-HYDROXIDE ION REACTION

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
Ralph Theodore Overman
A.B., Kansas State Teachers College, 1939
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ABSTRACT

This investigation is a part of a general program of research which has for its purpose the collection of data on dielectric and solvent effects in solution kinetics. In this particular study the mechanism of the alkaline fading of iodo phenol blue was under consideration. Also the electrostatics of the diacetone alcohol-hydroxide ion reaction was to be investigated, from the published data of Åkerlöf.

The experimental part consisted of studying the effect of adding sodium iodide to fading solutions of iodo phenol blue and of studying the absorption spectra of both the faded and unfaded dyes and also the absorption of the acid forms of both unfaded and regenerated dye.

The obedience of the kinetics to the requirements of the Debye-Hückel limiting law indicates that the sodium iodide is exerting the Brönsted primary salt effect upon the reaction rate. The absorption spectra of the faded iodo phenol blue closely resembling that of water indicates that a carbinol is formed during the fading process. This is further confirmed by the fact that the absorption of the acid forms of the unfaded and regenerated form of the dye are identical. This indicates the reversibility of the reaction.
and lends support to the carbinol formation theory of the fading process.

The electrostatic theory for reactions between ions and molecules was applied to Åkerlöf's data for the alkaline decomposition of diacetone alcohol with respect to the primary salt effect and the influence of the changing dielectric constant of the solvent. The theory was found to give reasonable results for the primary salt effect for all salts excepting fluorides, carbonates, and sulfates. In these cases, influences other than electrostatic were predominant.

The theory also gave the correct direction of change of the velocity constants with decreasing dielectric constant of the solvent over the range of 50-78.5 except for isopropyl alcohol mixtures. For methyl alcohol-water, glycerine-water, and glycol-water solvents a chemical influence in the same direction as the expected electrostatic effects magnified the constants used in plotting these data against the theoretical curve.
INTRODUCTION

Compared to thermodynamics and many other theoretical fields of chemistry the theory of reaction velocity is only in the beginning of its growth. It is increasingly evident, however, that principles are being developed which are satisfactory. These principles rest on the work of such men as Arrhenius, Brönsted, Debye, Hückel, and Scatchard.

The modern theory of electrolytes (8) predicts that the presence of electrical charges in reactions will affect the rate of the reaction in two ways. Considering the reaction to be essentially a function of collision, the presence of the charges may involve (a) the electrical attraction or repulsion between reactants and (b) the ionic atmosphere which disturbs the statistical distribution of the reactant ions as a function of all the ions in the system. It is possible, then, in some cases to determine the nature and mechanisms of reactions involving electrical forces from a study of their reaction rates.

Very pronounced influences upon the reaction rates are found to be changes in temperature which was early formulated by Arrhenius (9); the dielectric effect of the solvent which was studied by Warner and others (21) and the solvent effect which was investigated by Daniels (13).

In investigations carried on to determine the parts
played by these various factors one of the convenient reactions to be studied was that of the alkaline fading of several of the sulfonphthalein dyes. A controversy has consequently arisen in the literature as to the correct mechanism for this reaction. This present investigation is a study of various possible mechanisms which have been proposed for this fading reaction.

One of the most recent additions to the field of kinetics has been the development of satisfactory equations for the reactions between ions and dipolar molecules by Amis and Jaffé (7). It is also the purpose of this investigation to study some of the published data for the reaction of the alkaline decomposition of diacetone alcohol as an example of the above type of reaction.
a. Kinetics of ion-ion reactions

The foundation of modern kinetics lies in the fundamental work of Guldberg and Waage (15) in their formulation of the Law of Molecular Concentrations or, as it is usually called, the Mass Action Principle. This states as the fundamental concept the principle that the rate of a chemical reaction is proportional to the molecular concentrations of the substances involved in the reaction.

As experimental work became more nearly accurate, it became increasingly evident that there were other generalizations which could be made in the study of rates of reactions. Another classical generalization was made by Arrhenius (9) in his formulation of the equation involving the energy of reaction and the temperature coefficient given by

$$\frac{d \ln k}{dT} = -\frac{E}{RT}$$  \hspace{1cm} (1)

The integrated form containing the well-known $E$ constant of Arrhenius proved to be extremely useful in the next period of work since the equation was in accordance with nearly all the data that was extant at the time.

The next step in the development and classification of rate processes came in the formulation of the various
orders of reactions and the derivation of the concentration
dependance in the various orders then known. This placed
the kinetics of reactions on a mathematical basis in which
quantitative predictions could be made as to the rates
as functions of concentration of the reactants and of
temperature.

The work of Arrhenius was monumental in its results
for many reactions, but it was soon observed that the Mass
Law was not obeyed by strong covalent electrolytes unless
they were in very dilute solutions or by strong electrovalent
electrolytes. There were many phenomena which were not
in accord with the Arrhenius equation. There then
developed the conception of a partial ionization which
was fairly satisfactory in the explanation of such phenomena.

Debye and Hückel (14) derived equations which
satisfactorily explained a great many such phenomena
and may be considered another step in the broadening process
which the field is undergoing. They assume several things
including a Boltzmann distribution coefficient and Poisson's
law of charge density. Their reasoning considers that
because of an attraction between like charges and repulsion
between unlike charges a positive ion will be surrounded
by an "ionic atmosphere" in which there are on the average
more negative than positive ions. In a small element of
volume $dV$ around a point, at a given distance from the ion.
there will be on the average over an interval of time, more negative than positive ions. This tendency of the ions to arrange themselves in some kind of order in the solution is partially overcome by thermal agitation. Because of these opposing effects around a given ion there will be a potential field, $\Psi$, whose average value over a time interval will depend on the distance from the ion. According to the Boltzmann principle the ionic distribution is a function of the ratio of the electrical energy to the thermal energy such that in this volume $dV$ around the ion there will be

$$dn^+ = n^+ e^{-\frac{\epsilon \Psi}{kT}} dV$$
**positive ions**

and

$$dn^- = n^- e^{-\frac{\epsilon \Psi}{kT}} dV$$
**negative ions**

in which $\epsilon$ is the charge on an electron, $K$ the Boltzmann factor and $T$ the temperature.

This accounts, mathematically, for the fact that the tendency of the ions to arrange themselves in solution is increasingly opposed by thermal agitation since if $T$ is infinity,

$$\frac{\epsilon \Psi}{kT} = 0$$

then

$$n^+ = \frac{dn^+}{dV}$$

and

$$n^- = \frac{dn^-}{dV}$$

If then $n^+ = n^- = n$, the net charge per unit volume at a point where the potential is $\Psi$ is given by

$$\rho = \frac{\epsilon (dn^+ - dn^-)}{dV}$$

which by the Boltzmann principle becomes

$$\rho = n \epsilon \left( e^{-\frac{\epsilon \Psi}{kT}} - e^{+\frac{\epsilon \Psi}{kT}} \right)$$

(2)

If we expand this term and neglect higher powers when the
potential is small compared to the thermal forms of the forces, we arrive at the charge around any one ion of a given sign. Now using the relation of the potential $\psi$ to the charge density $\rho$ as given by the Poisson equation, we arrive at the equation relating the charge density and potential

$$\frac{1}{r^2} \frac{d}{dr} (r^2 d\psi) = \frac{\varepsilon \rho e^2}{D \kappa T}.$$  \hspace{1cm} (3)

Debye and Hückel then introduce the term kappa as defined by

$$\kappa = \sqrt{\frac{\varepsilon \rho e^2}{D \kappa T}}.$$  \hspace{1cm} (4)

This term has the dimensions of reciprocal length and is very important in the development of the theory. In this equation $\frac{1}{\kappa}$ is called the thickness of the ionic atmosphere.

On integrating the equation (3) from the distance of closest approach $a_1$ to infinity we get for the potential at the distance $a_1$

$$\psi = \frac{\varepsilon}{D a_1} \frac{1}{1 + \kappa a_1}$$

or expanding

$$\psi = \frac{\varepsilon}{D a_1} - \frac{\varepsilon \kappa}{D (1 + \kappa a_1)}$$

The equation may be written in the form

$$\psi = \psi_o + \psi_1$$

where

$$\psi_o = \frac{\varepsilon}{D a_1}$$ \hspace{0.5cm} and \hspace{0.5cm} $$\psi_1 = -\frac{\varepsilon \kappa}{D (1 + \kappa a_1)}$$

$\psi_o$ is the potential at the surface of the ion due solely to the charge on the central ion itself and is independent of the ion concentration.
The quantity, \( \psi \), is the total potential due to the ionic atmosphere or the potential due to the arrangement of the surrounding ions in the vicinity of the given ion and is a function of the concentration.

From thermodynamics we can obtain the free energy of a cell as a function of the effective concentration of the concentration cell which is defined by Lewis and Randall as the concentration times an activity coefficient \( \bar{f} \). This may be given for a cell of active concentration as \( c_1 \times f_1 \) and for another cell of active concentration of \( c_2 \times f_2 \), as

\[
\Delta F = 2RT \ln \frac{c_1 f_1}{c_2 f_2}
\]

or

\[
\Delta F = 2RT \ln \frac{c_1}{c_2} + 2RT \ln \frac{f_1}{f_2} \quad (7)
\]

If solutions are ideal the first term of the right side of equation (7) is sufficient; but for real solutions the second term takes care of the departure from ideal.

Since equation (4) shows that kappa depends on the square root of the number of ions per unit volume, the value of \( \psi \) is a function of the concentration. On the other hand the portion of the potential due to the ion itself is the same in both the dilute and concentrated solution. The change in electrical energy corresponding to this potential accompanying the discharging of the ion is therefore equal and opposite to that accompanying the charging process of the ion so we need consider only
the excess potential \( \Psi_1 \) due to the ion atmosphere.

From the electrical energy in charging and discharging an ion we can get the equation

\[
\Delta F_{\text{elect.}} = RT \ln f = \frac{-e^2 q}{2D(1 + \varepsilon a_i)}
\]

This equation, for any given solvent and temperature, on the introduction of the proper constants takes the form of the first approximation of Debye and Hückel (14) for univalent electrolytes

\[
- \log f = \frac{a \sqrt{c}}{1 + \varepsilon a_i c}
\]

When the concentration is very low, then \( \varepsilon a_i c \) becomes negligible compared to unity and equation (2) takes the form of the Debye-Hückel limiting law

\[
- \log f = a \sqrt{c}
\]

Using an analogous procedure it is also possible to derive expressions for multiply-charged ions which contain a term involving the square of the valence \( z \) of the ion and in which case the limiting law for multiply-charged ions is of the form

\[
- \log f_i = a_i^2 a \sqrt{c}
\]

showing that for any ion the activity coefficient is a function of the square of the valence.

There are several limitations and criticisms of the theory which may be briefly enumerated: (a) the expansions for the charge densities were approximated by dropping terms
which must be considered in the range of applicability; (b) the Boltzmann distribution for $\Psi$ gives an average value which is subject to side fluctuation; (c) at high concentrations the dielectric constant of the solvent may change because of the presence of charged ions consequently it is usual to use a macroscopic dielectric constant to conform to Coulomb's law; (d) the value of $a_1$ applied has a minimum below which the equation will not hold, which value is not necessarily the calculated distance of closest approach; (e) it successfully accounts for the experimental results when its application is limited to solutions in which the ratio of the electrical to the thermal energy is small, i.e. $\frac{e\Psi}{kT} \ll 1$.

It follows from the equations that the potential is small if the dielectric of the solvent ($D$) is high, if the ions are large, (large $r$), or if the charge on the ion is low.

The Debye-Hückel theory holds for the ionized part of electrolytes, and since no "degree of dissociation" has been introduced it holds for 100% ionization.

Brönsted (11) in 1922 introduced another concept into the picture dealing with the nature of the reaction between any two ions. This theory was brought about by a study of the part played in reaction rates by the addition of neutral salts. He distinguished between two distinct effects which salts may have on reaction rates: (a) primary salt effect which is purely a kinetic effect confined to the reaction ions in which there is a change of activity due to the addition of an electrolyte; (b) the secondary salt
effect produced by a shift in the degree of dissociation
of a weak electrolyte based on the Mass Action Law, then
one of its ions is involved in the kinetic process.

Brönsted assumes that reactions go through an
intermediate complex as in the equation

\[ A + B \rightleftharpoons X \rightarrow C + D. \]

At equilibrium by the Mass Action Law he writes for the
initial step

\[ k = \frac{[X]}{[A][B]} = \frac{[X]}{[A][B]} \frac{f_X}{f_A f_B} \quad (12) \]

Then the velocity of formation of the complex is
given by

\[ \text{velocity} = k' \frac{[X]}{[A][B]} = k' \frac{[A][B]}{f_A f_B} \quad (13) \]

or by letting \( k_0 = k'k \) this becomes

\[ \text{velocity} = k_0 c_A c_B \frac{f_A f_B}{f_X} \]

The complex \( X \) is elusive and cannot be isolated but the
rate depends on its specific reactivity \( k' \) and \( k \) is therefore
independent of temperature. If the life of the complex
is long compared to the time between two activating
collisions, then it is probably correct to assume that the
purely physical collision complex determines the rate of
the reaction through a spontaneous monomolecular decomposition
induced by thermal agitation. However, if the life of
the complex is short, \( T \) exerts its effect through the
equilibrium constant, and Brönsted (11) is probably correct
in his hypothesis that reaction velocity is determined by
the difference in the potential of the initial and critical states of the reacting systems but is independent of the potential of the final state of the system. This is equivalent to saying that the rate of reaction depends upon the ratio of the activity coefficients of the substances in the initial and critical states.

Scatchard (20) arrives at the same conclusion by evaluating the Brönsted activity factor

\[ F = \frac{f_A f_B}{f_X} \]  

(14)

using the assumption that a statistical relation is also involved in thermodynamic equilibria. He thus obtains the Brönsted equation (15)

\[ k = k_0 \frac{f_A f_B}{f_X} \]

in which k is the observed rate constant and \( k_0 \) is the ideal rate independent of charges. Hence F is a measure of the deviation of k from the ideal \( k_0 \).

Scatchard then proposes three conditions for a reaction, the rate being determined by these factors:

(a) the ions must approach to a certain distance; (b) the ions must have a relative orientation which is, however, not critical; and (c) the energy must be localized or the molecule must be deformed to let the ions approach to the proper energy level.

This derivation by Scatchard of the Brönsted theory ranks as one of the great contributions to solutions kinetics,
together with the other developments already mentioned. Each of the conditions of reactions given above can be considered of some importance in evaluating the final rate constant. It is possible that the molecules must remain in this state during a very short but finite time necessary for reaction. It is possible also that there are two or more states, quite different in some respects, which lead to the same reaction. These conditions seem general enough to cover all cases. If the approach of the molecules follows the reception of energy and the deformation and orientation, there is a "reaction on collision"; if the approach precedes any of the other steps, there is a preliminary complex formation. Scatchard believes that it is of no importance whether this complex is to be regarded as a "physical constellation" or a "chemical compound" since the distinction depends on the definition of a compound. It seems equally unimportant whether the rate be calculated from the concentration of reacting complexes or from the number of collisions with the necessary orientation and energy, multiplied by a factor for the duration of the collision.

For reactions slow enough to be measured, the reacting state is a very improbable one. We must assume that it differs only slightly from other states whose total probability is very much greater than that of the reacting complex and which are in statistical equilibrium.
We may then treat the reacting complex as though it also were in equilibrium.

Brønsted's theory follows from Scatchard's assumptions without any use of statistical mechanics other than the general postulate that statistical equilibrium implies thermodynamic equilibrium. Scatchard's work is made necessary by the fact that thermodynamics tells us nothing of the value of $\Omega$, the activity coefficient of a complex, that disappears as soon as it is formed and whose amount can never be measured. The only methods of treatment are the use of empirical generalizations or statistical mechanics as done by Scatchard. Its application is limited to ion-ion reactions and to cases where we may use Debye-Hückel radii of closest approach since Brønsted calculated that ionic reactions depend only on the valence type.

Scatchard follows the procedure of Christiansen (12) in calculating the concentration of the complex directly from the equations of Debye and Hückel. This concentration is proportional to the bulk concentration of $A$ molecules multiplied by the average concentration of $B$ molecules at a distance $r$ from an $A$ molecule, where $r$ is the distance of approach characteristic of the complex. According to Debye and Hückel this is given by

$$c_x = k'' c_A c_B \exp \left( -\frac{\psi}{kT} \frac{r^2}{\varepsilon} \right)$$

(15)
From equation (15) for the mean potential at a distance \( x \) from \( A \) and the equation for the concentration of the complex we have

\[
c_x = k^n c_{AB} e^{-\frac{e^2 z_A z_B}{D kr}} \frac{e^{-\frac{k^2 a_i}{1 + K a_i}}}{1 + K a_i} \tag{16}
\]

When kappa equals zero the equation becomes

\[
c_x^0 = k^n c_{AB}^0 e^{-\frac{e^2 z_A z_B}{D kr}}
\]

or

\[
\frac{c_x^0}{c_{AB}^0} = k^n e^{-\frac{e^2 z_A z_B}{D kr}} \tag{17}
\]

It follows then that by combining the equations (16) and (17)

\[
\ln \frac{f_{AB}}{f_x} = \ln \frac{c_x}{c_{BA}} - \ln \frac{c_x^0}{c_{AB}^0} = \frac{e^2 z_A z_B}{D kr} \left[ 1 - e^{-\frac{k^2 a_i}{1 + K a_i}} \right] \tag{18}
\]

It is to be noticed that Satchard has introduced the Boltzmann factor, since the rate must depend on the forces that bring the ions together (potential \( x \) charge) and those that tend to keep them apart (temperature). However, he did not go through the process of thermodynamic integrations used by Debye and Hückel. By making necessary expansions and limitations, the equation of Satchard can be made identical to that of Brönsted.

If we choose a reference state we are able to obtain the important effect of dielectric constant of the solvent on the reaction rate. If we choose for the reference state of the solvent the concentration at which all ionic forces have been eliminated, we have the following:

\[
\ln \frac{f_{AB}}{f_x} = \ln \left( \frac{c_x^0}{c_{AB}^0 c_B} \right) - \ln \left( \frac{c_x^0}{c_{AB}^0 c_B} \right) = 0
\]
This effect of the dielectric constant of the solvent is very important and comes directly from Scatchard's derivation of the Brönsted activity factor.

Now in extending the work of Scatchard it is possible to take into account those cases where the environment of the reaction changes continuously; that is, the ionic strength is actually changing while the reaction is taking place.

The treatment is based on the Brönsted "critical complex" X with the rate of formation occurring as in equation (13). On substituting the various constants in equation (9) for a charged ion the Debye-Hückel expression for the activity coefficient of an ion in water at 25°C is

\[
- \log f_1 = \frac{1.16 \ z_1^2 \ \sqrt{u}}{1 + 0.328 \ a \ \sqrt{u}}
\]  

(20)

The numerical constants vary with the temperature and dielectric constant of the solvent. For ionic strengths of very low value or for very dilute solutions we have

\[
- \log f_1 = 1.16 \ z_1^2 \ \sqrt{u}
\]  

(21)

For the Bronsted activity factor (Equation 8) assuming the same size for all the ions we obtain

\[
\log \frac{f_{A\beta}}{f_x} = \frac{2.32 \ z_1^2 \ \sqrt{u}}{1 + 0.328 \ a \ \sqrt{u}}
\]  

(22)

This equation upon which a fundamental part of this research is based expresses tacitly that an addition of salt (a) increases the rate of a reaction for ions of like signs and
(b) decreases the rate for ions of unlike signs, because the $z_A z_B$ term is then negative and consequently the rate is decreased. It also shows that the rate should have no primary salt effect for a reaction between an ion and a neutral molecule. These are the conclusions drawn by Brønsted. Brønsted’s application is limited to reactions where the ionic strengths do not change and therefore ones is which the activity coefficients are constants during the course of the reaction. Extension has been made of the above equation to reactions of changing ionic strength based on an additional factor to include the changing of the ionic strength in the solution. This factor is of the form

$$u = u_0 \sqrt{1 + g x}$$

where $u_0$ is the initial ionic strength, $x$ is the extent of the reaction and $g$ is a constant.

Combining the results of Brønsted, (11) Christiansen (12), and Scatchard (20), the general kinetic equation may be formulated as follows

$$\ln k = \ln k_\infty - \frac{z_A z_B e^2}{D K T} \frac{1}{r_A + r_B} + \frac{z_A z_B e^2}{D K T} \frac{1}{1 + \kappa}$$

where $k_\infty$ is the reaction rate extrapolated to infinite dielectric constant and to zero ionic strength; the term $r_A + r_B$ is the radius of the Brønsted complex and kappa is defined as in equation (4).

Another step in the extension of the theory was made by Warner (21), LaMer (18), and others in the derivation
of energies of activation and entropies of activation. Considering the rate of a given reaction to be a function of the temperature and the dielectric of the solvent we may write

\[ \frac{\partial \ln k}{\partial T} dT + \left( \frac{\partial \ln k}{\partial \epsilon} \right) d\epsilon \]  

By use of the Arrhenius equation (1) we may derive expressions for the energies of activation as a function of composition and dielectric by transforming equation (25) into terms involving energies of activation and terms involving the change of rate with dielectric constant.

The Arrhenius equation may be integrated in two ways, one, by integration between the limits \( T_1 \) and \( T_2 \); the other, by introducing a constant of integration \( B \) which is a factor involving a frequency of collision and an entropy of activation as defined by LaMer (18). The equations may be shown to be the following by the use of limits

\[ \Delta E^* = \frac{2.303 \ R \ T_2 \ T_1 \ \log k_2}{T_2 - T_1} \]  

or introducing the constant of integration

\[ \log k = B - \frac{\Delta E^*}{2.303 \ R} \]  

from which we may get for \( B \) using the rates at two temperatures

\[ B = \frac{T_2 \ \log k_2 - T_1 \ \log k_1}{T_2 - T_1} \]  

From thermodynamic considerations involving specific heats it can be shown that \( B \) is of the form

\[ B = B^0 + \frac{\Delta E^*}{2.303 \ R} \]
in which $B_0$ is the logarithm of a frequency of collision as
derived for reactions taking place in the gas phase and $\Delta S^*$
is the entropy of activation of the reaction.

LaMer then shows that both the $\Delta E^*$ and $\Delta S^*$ are complex
being of the form

$$\Delta E^* = \Delta E^*_0 + \Delta E^*_D + \Delta E^*_in$$  \hspace{1cm} (30-A)

and

$$\Delta S^* = \Delta S^*_0 + \Delta S^*_D + \Delta S^*_in$$  \hspace{1cm} (30-B)

in which the $o$ state is the uncharged effect of the reacting
particles, the $D$ term being due to the electrical charge on
the reactants, and the $in$ term being due to the interaction
of the ionic atmospheres for reactions between ions.

Following the procedure of LaMer and Kammer (18) in
considering the effect due to the ionic atmosphere of the
reactants, the following expressions may be derived for the
values of the energy of activation due to the atmosphere and
of the entropy of activation due to the atmosphere:

$$\frac{\Delta E^*_in}{2.3 R T} = - \frac{2 z AZRB \sqrt{u}}{(DT)^{1/4}} \left[ \frac{3}{2} \frac{\ln D}{\ln T} + \frac{1}{2} \frac{\ln V}{\ln T} + \frac{1}{2} \right]$$  \hspace{1cm} (31-A)

and

$$\frac{\Delta S^*_in}{2.3 R} = - \frac{2 z AZRB \sqrt{u}}{(DT)^{1/4}} \left[ \frac{3}{2} \frac{\ln D}{\ln T} + \frac{1}{2} \frac{\ln V}{\ln T} + \frac{1}{2} \right]$$  \hspace{1cm} (31-B)

By using these equations the theoretical slope may be
determined if we plot $\Delta E^*$ against $\sqrt{u}$ and the $B$ value against $\sqrt{u}$.

The agreement in observed values for ion-ion reactions
has thus far been exceedingly good except for what might
be considered specific solvent effects. For ion-ion reactions
equation (24) is considered adequate although an important term involving a temperature dependence factor has recently been derived by Amis and Jaffe (6) which explains some of the anomalies observed involving the temperature terms in the rate calculations.

This work has been culminated by Eyring who was the first to calculate the actual rate of a chemical reaction from a knowledge of the potential energy of the reacting systems in the cases where such information is available (23).

b. Reactions of the fading of iodo phenol blue.

In the literature there have been presented two different mechanisms for the alkaline fading of the phenol-sulfonphthalein dyes. Thiel (22) and others (5, 16,17) have considered the fading reaction as an addition of an hydroxide ion to the dye ion to form a colorless carbinol. This would be given by the following equation:

\[
\text{Reaction I: } \quad \text{C}-\text{OH}^- + \text{OH}^- \rightarrow \text{C}-\text{OH}^-\text{I}^-\text{O}^-
\]

Kilpatrick (19) with Panepinto, however considers the reaction as being a substitution of an hydroxide ion for one of the iodine atoms yielding iodide ion the solution. Their reaction would be represented by the following equation:

\[
\text{Reaction II: } \quad \text{C}-\text{OH}^- + \text{OH}^- \rightarrow \text{C}-\text{OH}^-\text{I}^-\text{O}^-
\]
We propose to test the mechanism by two methods.

I. According to the general kinetic equation (24) for ion-ion reactions, the effect of an added electrolyte would be to increase the rate of fading since the ions involved are of like sign. It is fortuitous in this case that the ions under discussion are the negative iodide ion and the negative hydroxide ion. According to the equation, then, the addition of a neutral salt to the reaction between two negative ions should increase the rate a calculable amount. On the other hand, if the reaction is of the type indicated by Kilpatrick and involves the breaking off of an iodide ion, the mass action effect of adding a substance containing a common ion such as sodium iodide would be such as to measurably decrease the reaction rate.

II. The alkaline form of iodo phenol blue has a characteristic absorption curve whose intensity is a function of the concentration of the dye present in the blue form. An examination of the spectra in the blue and faded forms should yield information as to what possible structures are present. According to Brode, (10) the quinoid structure has a characteristic absorption band at a more or less definite region of the spectrum depending on the other groups present. If the fading reaction occurs simply as a substitution of an hydroxide ion for an iodide ion (reaction II), the only difference in the spectra of the unfaded and faded forms should be a slight difference in the weighting of the groups.
or should involve only a slight displacement in the absorption band. If the fading is caused by a complete destruction of the quinoid linkages and the formation of other groups, the faded spectrum should have the characteristic form of the new groups. In the case of the reaction of Thiele (reaction I) the only absorption should be caused by the carbimol, the phenol, and the sulfonic acid groups which have no absorption in the range of a normal photographic plate (10).

The reaction is also known to be quantitatively reversible (8). The addition of large quantities of acid reverses the reaction to give a compound resembling the original unfaded dye molecule in that it undergoes the characteristic indicator changes as a function of pH. Again it is possible to investigate the structures spectrographically. If the fading is a rearrangement according to reaction I, the regeneration involves simply a re-formation of the molecule into the original form. The spectrum of the regenerated dye should then be identical to that of the original molecule.

It would seem highly improbable that the acidification of a solution containing the faded quinoid form as in reaction II would replace the iodide ion in the phenol nucleus which would be necessary when the reverse action takes place.
EXPERIMENTAL

The materials and methods used in these studies were essentially those used by Amis and LaMer (8) in similar researches. The purification of the reagents and preparation of solutions was that given by them. The iodo phenol blue was prepared in stock solutions which were $1 \times 10^{-4}$ molar as described by these authors. The sodium hydroxide was also made up and standardized in a similar manner. The sodium iodide (C. P. Baker's analyzed) was made up before each run on a gravimetric basis, diluted to a suitable volume and divided into aliquot parts on a volumetric basis.

All volumetric apparatus and weights were calibrated. The temperatures were held constant to $\pm 0.01^\circ C$.

Ten milliliters of the $1 \times 10^{-4}$ molar stock solution of iodo phenol blue were placed in a volumetric flask and sufficient sodium iodide solution, sodium hydroxide solution and water were added to make a total volume of 100 milliliters which was $1 \times 10^{-5}$ molar with respect to the dye, 0.006 molar with respect to the sodium hydroxide and with varying concentrations of sodium iodide to reach the other ionic strengths used in the studies. The time of addition of NaOH was noted and used as the initial time in the runs. A standard neutral solution of unfaded dye was also made up and placed in the thermostat.

To make a reading five milliliters of the fading dye
solution were pipetted into one of the colorimeter cups and five milliliters of the standard unfading dye was placed in the other. Using a Klett colorimeter the amount of fading was determined as a function of time. The illumination used was a Mazda lamp with a blue filter.

The spectrographic data were obtained using a large Littrow spectrograph with spectrophotometric attachments. For these experiments dye solutions were made up to $10^{-5}$ molar as in the kinetic runs. Enough of the solution was pipetted out to fill a fused quartz absorption cell. All measurements were made from cells with a column of absorbing medium which was 2 cm. in length. The light source for the visible was a Mazda ribbon filament lamp and for the ultraviolet was a hydrogen discharge tube. The setting for the visible spectra was position #3 of the glass system covering a frequency of 450-700 fresnel units. For the ultraviolet readings on the absorption of the faded dye, positions #5 and #9 of the quartz system were used covering a region of 430-1500 fresnel units or from 2000-6000 Å.

The procedure consisted of printing a millimeter scale on the plate, exposing the plate as a blank with no absorption cells in the light beam, and then interposing the cells, one being filled with distilled water and the other containing the sample being studied. The blank was made necessary by the fact that it was found to be impossible to equate the light intensities of the two parts of the beam visually so that they gave identical readings on the densitometer.
The correction could then be made for initial differences in intensity of the two beams. The time of exposure was 3, 4, and 5 seconds—the final curve being plotted for the average of the three densitometer readings corresponding to a given frequency.

The densitometer used was a Hardy Electric Company instrument which measures the density of the plate by use of a photoelectric cell. In this instrument the dark current is set to zero on the galvanometer scale and the reading of 100 as the transmission through a clear portion of the plate. In this case the densitometer reading (D) ranged from zero to one hundred with the reading being inversely proportional to the density of the plate and directly proportional to the amount of light absorbed by the dye at a given frequency.

The logarithm of the ratio of the galvanometer deflections for the beam which had passed through the dye (D) to that for the beam which had passed through the water (D₀) is then proportional to the absorption of the incident light by the dye solution when proper corrections are made for the deflections, D' and D₀', obtained for the blank. From this we calculated the specific extinction coefficient \( \kappa \). According to Beer's Law

\[
\log \frac{I}{I_0} = -\kappa cd = \log \frac{D_0}{D} - \log \frac{D_0'}{D'}
\]

Then the specific extinction coefficient, \( \kappa \) is
calculated for our experiments as

\[ k = \frac{1}{\text{od}} \log \frac{D_D'}{D_0 D'} \]

and is of the units of grams per liter centimeters. This is plotted against frequency according to the suggestion of Brode (10).
DATA

The rate constants of iodo phenol blue in alkaline solution were calculated from the equation

\[ \log k = \frac{1}{t} \log \frac{a}{a-x} \]

The value of \(a\) was represented by the reading, on the colorimeter before any fading took place. The value \(a-x\) was represented by the reading (at the time, \(t\)) of the fading dye against the standard on the colorimeter.

The true bimolecular rates were obtained by dividing the pseudo-uni-molecular rate constant by the concentration of the hydroxide ion which because of its large excess remained sensibly constant throughout the run. The units chosen were moles per liter for the concentration, and days as the time unit.

In Table I are given typical examples of the data of the kinetic runs. These are given as the true bimolecular rate constants \(k\) and calculated from the pseudo-uni-molecular rate constants by dividing by the concentration. The concentration units are moles per liter with the time expressed in days.

The values indicate a primary salt effect with increasing concentration of sodium iodide added, as is illustrated in Table II, where the constants are recorded as a function of the ionic strength at the three temperatures, 25\(^\circ\)C, 35\(^\circ\)C, and 45\(^\circ\)C. The quantitative agreement of the data
with Bronsted's theory of the primary salt effect is illustrated in Fig. 1, where $\log k$ is plotted against the square root of the ionic strength for the three temperatures indicated. The Debye-Hückel limiting law is represented by the straight lines and the data by the circles.

The agreement is all that could be desired almost throughout the range of concentrations studied. In fact the agreement reaches to readings of ionic strengths greater than would ordinarily be expected, but does correspond to the primary salt effect observed by Amis and LaMer for the fading of brom phenol blue in different concentration of sodium hydroxide and also for the fading of iodo phenol blue as observed by Panepinto and Kilpatrick for different concentrations of electrolyte. There is no indication that the mass action is influential in the observed kinetics with added sodium iodide. It would seem extremely improbable that the mechanism is a replacement of iodine by a hydroxide ion in the dye molecule thus producing iodide ion.

Table II also contains the energies of activation and the Arrhenius frequency factors at different ionic strengths and for the three specified temperatures. From equation (31-A) the slopes for the energies of activation as a function of ionic strength for the fading reaction are 1569 and 1605 for 30° and 40° C. respectively. This gives for these data the equations

$$\Delta F^*_{30} = 1569 \sqrt{u}$$

$$\Delta F^*_{40} = 1605 \sqrt{u}$$
In Fig. 2 the energies of activation are plotted as a function of the \( \sqrt{\bar{u}} \). Again the solid lines represent the Debye-Hückel limiting law slope and the circles represent the data. When it is considered that an accuracy even as great as 100 calories is considered good in the measurement of energy of activation it will be seen that the data conforms to the theory as well as could be expected. This increment of energy of activation with increasing ionic strength represents that part contributed by the ionic atmosphere to the energy of activation between ionic reactants as represented by Equation (31-A).

The degree to which the Arrhenius frequency factor \( B \) conforms to electrostatic theory is illustrated in Fig. 3. The slopes of these lines were evaluated from Equation (31-B) and are respectively 3.19 and 3.25 for 30 and 40 degrees respectively. That is, we may represent equation (31-B) for these data by the two following equations:

\[
\frac{\Delta \theta_{30}^*}{2.3 R} = 3.19 \sqrt{\bar{u}}
\]

\[
\frac{\Delta \theta_{40}^*}{2.3 R} = 3.25 \sqrt{\bar{u}}
\]

Again the increment of the Arrhenius factor \( B \) with ionic strength represents the contribution of the ionic atmosphere to this factor as given by equation (31-B). The slope of the Debye-Hückel limiting law averages these data fairly well, as can be seen from Fig. 3. The slopes for
the contribution of the ionic atmosphere to the energy of activation and the frequency factors were calculated for the mean of the temperatures and dielectric constants of the solvent used in making the kinetic runs which determined these energies of activation and frequency factors.

In Table III we give the specific extinction coefficient and the corresponding wavelengths of the unfaded iodo phenol blue in $10^{-5}$ molar dye solution in neutral solution. In Fig. 4 this data is plotted using frequency in fresnel units as abscissae with specific extinction coefficients as ordinates. This method of plotting corresponds to decreasing wavelengths of light from left to right on the abscissae thus making the red end of the spectrum on the left. The dye is seen to have a sharp absorption maximum at a frequency of 510 f. or 5808 Å. Now if the fading mechanism were one of substitution of a heavier iodide ion by a lighter hydroxide ion there should be only a shifting of the absorption band to correspond to the difference in resonance of the molecule. The absorption maximum however would still be in the visible. However, in Table IV we give the specific extinction coefficient as a function of frequency for the alkaline faded iodo phenol blue. The data is plotted in Fig. 5. This absorption spectrum is typical of non-chromophoric molecules and would correspond to that obtained for only those molecules which contain linkages similar to those found in alcohol, acids,
and water. The evidence from absorption spectra would indicate that the fading process is one in which the quinoid structure of the iodo phenol blue is replaced by the carbinol which would have complete transmission in the visible. Further evidence on the mechanism can be obtained from the absorption of the acid form of the iodo phenol blue. Amis and LaMer (8) observed that the faded dye when acidified gradually regained the acid color of the unfaded dye. This regeneration has also been found to be quantitative in relatively large concentration of the acid. If the regenerated dye is exactly the same as the unfaded material then the acid regeneration means that the hydrogen ion has the ability not only to remove the hydroxyl ion but also to quantitatively replace the iodide if the mechanism for the fading proposed by Kilpatrick, et al., is accepted. On the basis of the mechanism proposed by Thiele and others, the acid regeneration would mean merely the removal of the hydroxide ion in the carbinol and the reforming of the quinoid structure in the dye. It is very improbable that iodide ion could be made to enter a benzene nucleus by mere acidification of a solution of a material in which substitution is to take place.

In Table V is given the specific extinction coefficient as a function of frequency of both the unfaded and regenerated iodo phenol blue; the measurements being taken in acid solution of like concentration in both cases.
These data are plotted in Fig. 6. In the figure the symbol X represents the absorption of the unfaded and the e the absorption spectrum of the regenerated dye. It can be seen that the two spectra are identical and hence, the regenerated dye corresponds exactly to the unfaded material. This would indicate that the regeneration process is merely a change from the colorless carbinol to the yellow acid quinoid structure of the iodo phenol blue.
**TABLE I**

**SAMPLE RUNS**

Kinetics of the Fading of Iodo Phenol Blue in Water

<table>
<thead>
<tr>
<th>NaOH, 0.006 N.</th>
<th>NaI, 0.002 N.</th>
<th>NaOH, 0.006</th>
<th>NaI, 0.002</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Days</th>
<th>$10^5 x$ conc. of I. P. B.</th>
<th>k.</th>
<th>Days</th>
<th>$10^5 x$ conc. of I. P. B.</th>
<th>k.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.896</td>
<td>0.903</td>
<td>20.9</td>
<td>0.874</td>
<td>0.679</td>
<td>73.9</td>
</tr>
<tr>
<td>1.031</td>
<td>0.878</td>
<td>20.8</td>
<td>1.041</td>
<td>0.630</td>
<td>73.8</td>
</tr>
<tr>
<td>2.113</td>
<td>0.766</td>
<td>20.8</td>
<td>1.667</td>
<td>0.451</td>
<td>73.8</td>
</tr>
<tr>
<td>2.567</td>
<td>0.725</td>
<td>20.7</td>
<td>1.870</td>
<td>0.434</td>
<td>74.0</td>
</tr>
<tr>
<td>3.000</td>
<td>0.687</td>
<td>20.9</td>
<td>2.030</td>
<td>0.404</td>
<td>74.0</td>
</tr>
<tr>
<td>4.000</td>
<td>0.609</td>
<td>20.7</td>
<td>2.500</td>
<td>0.329</td>
<td>73.9</td>
</tr>
<tr>
<td>5.000</td>
<td>0.540</td>
<td>20.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ave. 20.8  
Ave. 73.9
### Table II

Data for Water with Alkali-Hydroxide and Alkali Salt Added

Dye $10^{-5}$ M., NaOH 0.006 N. with added NaI

<table>
<thead>
<tr>
<th>$u$</th>
<th>$u$</th>
<th>$k$</th>
<th>$k$</th>
<th>$k$</th>
<th>$k$</th>
<th>$k$</th>
<th>$k$</th>
<th>$k$</th>
<th>$k$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.0000</td>
<td>(14.3)</td>
<td>(27.7)</td>
<td>(50.2)</td>
<td>12.070</td>
<td>11.520</td>
<td>10.00</td>
<td>9.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.006</td>
<td>0.0775</td>
<td>19.7</td>
<td>38.5</td>
<td>69.9</td>
<td>12.180</td>
<td>11.640</td>
<td>10.24</td>
<td>9.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.008</td>
<td>0.0825</td>
<td>20.8</td>
<td>40.6</td>
<td>73.9</td>
<td>12.190</td>
<td>11.560</td>
<td>10.23</td>
<td>9.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>0.1000</td>
<td>21.6</td>
<td>42.2</td>
<td>76.9</td>
<td>12.210</td>
<td>11.650</td>
<td>10.32</td>
<td>9.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.012</td>
<td>0.1096</td>
<td>22.6</td>
<td>44.2</td>
<td>80.6</td>
<td>12.230</td>
<td>11.700</td>
<td>10.34</td>
<td>9.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td>0.1265</td>
<td>24.0</td>
<td>47.0</td>
<td>86.0</td>
<td>12.250</td>
<td>11.750</td>
<td>10.37</td>
<td>10.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.026</td>
<td>0.1613</td>
<td>27.6</td>
<td>53.9</td>
<td>99.2</td>
<td>12.290</td>
<td>11.780</td>
<td>10.41</td>
<td>10.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE III

Absorption Spectrum of the Blue Form of Iodo Phenol Blue

Setting # 3, Using Glass Prism with Litrow Spectrograph

<table>
<thead>
<tr>
<th>Frequency (Fresnel units)</th>
<th>Wave Length (µ)</th>
<th>Specific Extinction Coefficient k</th>
</tr>
</thead>
<tbody>
<tr>
<td>461</td>
<td>650</td>
<td>6.3</td>
</tr>
<tr>
<td>476</td>
<td>630</td>
<td>5.4</td>
</tr>
<tr>
<td>493</td>
<td>600.8</td>
<td>31.1</td>
</tr>
<tr>
<td>510</td>
<td>580.8</td>
<td>64.5</td>
</tr>
<tr>
<td>524</td>
<td>570.2</td>
<td>47.5</td>
</tr>
<tr>
<td>537</td>
<td>550.9</td>
<td>26.2</td>
</tr>
<tr>
<td>552</td>
<td>540.3</td>
<td>20.0</td>
</tr>
<tr>
<td>578</td>
<td>510.9</td>
<td>7.6</td>
</tr>
<tr>
<td>603</td>
<td>490.7</td>
<td>4.0</td>
</tr>
<tr>
<td>627</td>
<td>470.8</td>
<td>4.2</td>
</tr>
<tr>
<td>647</td>
<td>460.4</td>
<td>3.7</td>
</tr>
<tr>
<td>668</td>
<td>440.9</td>
<td>5.1</td>
</tr>
<tr>
<td>688</td>
<td>430.6</td>
<td>4.4</td>
</tr>
</tbody>
</table>
TABLE IV

Absorption Spectrum of Faded Iodo Phenol Blue

Range 1500 f. to 430 f.  
(2000-6000 A°)

Settings # 5 and # 9 with Quartz Prism in Littrow Spectrograph

<table>
<thead>
<tr>
<th>Random Points taken over Range of 430-1500 f.</th>
<th>Specific Extinction Coefficient $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.8</td>
</tr>
<tr>
<td>2</td>
<td>4.9</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
</tr>
<tr>
<td>4</td>
<td>4.8</td>
</tr>
<tr>
<td>5</td>
<td>3.7</td>
</tr>
<tr>
<td>6</td>
<td>4.4</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
</tr>
<tr>
<td>Frequency (Fresnel units)</td>
<td>Specific Extinction Coefficient $k$ (unfaded)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>461</td>
<td>1.04</td>
</tr>
<tr>
<td>493</td>
<td>2.11</td>
</tr>
<tr>
<td>524</td>
<td>1.04</td>
</tr>
<tr>
<td>552</td>
<td>1.88</td>
</tr>
<tr>
<td>578</td>
<td>2.41</td>
</tr>
<tr>
<td>603</td>
<td>11.5</td>
</tr>
<tr>
<td>627</td>
<td>18.8</td>
</tr>
<tr>
<td>647</td>
<td>18.1</td>
</tr>
<tr>
<td>668</td>
<td>22.7</td>
</tr>
<tr>
<td>688</td>
<td>20.7</td>
</tr>
<tr>
<td>697</td>
<td>19.4</td>
</tr>
</tbody>
</table>
Log $K_{35} = \log K_{\text{scale}} + 0.20$

Log $K_{45} = \log K_{\text{scale}} + 0.40$
Fig. 2
CONCLUSIONS

1. The influence upon the kinetics of fading of iodo phenol blue of added sodium iodide is proved to be that of the Bronsted primary salt effect rather than a mass action effect.

2. Absorption spectrum data on the alkaline faded iodo phenol blue shows that the absorption corresponds to alcohols, acids, or water. This would be expected if the carbinol was formed during the fading process.

3. Absorption spectra of the unfaded and regenerated acid form of the iodo phenol blue are identical and hence, the fading process is reversed in acid solution.

4. These observations lead to the conclusion that the fading process is one of carbinol formation with the corresponding disappearance of the quinoid structure.

5. The data of Åkerlöf on the diacetone alcohol-hydroxide ion reaction both as to the effect of neutral salts and changing dielectric of solvent have been discussed in relation to the predictions of electrostatics theory for reactions between ions and dipole molecules.
APPENDIX

Kinetics of Ion-Dipole reactions

The equations given in the preceding section are totally inadequate in the study of ion-molecule reactions. This arises from an examination of the general equation (24) which is seen to involve terms considering in each case the valency of the two reacting units. Obviously, if one of the reactants has a valence of zero the agreement could in no wise be satisfactory. This has been shown by Amis and Jaffe (7) who have derived an equation for this type of reaction. Contrary to the conclusion that in a molecule-ion reaction there were no electrostatic forces between the ions and molecules except those of the ion, it has been shown that the molecule must be considered as a dipole because of the definite charge centers of these dipole molecules. This force is then a function of the dipole moment of the molecule, $\mu^*$, and of the angle of approach, $\theta$, of the reaction units in addition to the other factors outlined above for ion-ion reactions. Their equation is

$$\ln k = \ln k_{k=0} + \frac{\epsilon z \cos \theta (\mu^*_D - \mu^* e^{ikr_0})}{DKTr (1 + kr_0)}$$

(32)

This equation for ion-dipole reactions corresponds to equation (24) for the case of ion-ion reactions. In general,
the cosine \( J \) is chosen to be 1 and also the assumption is made that the critical distance \( r_0 \) corresponds to the radius of closest approach in the above equations.

Introducing the dimensionless variable

\[
z = \kappa a = \kappa r_0
\]

and the dimensionless quantity

\[
W = (\ln k - \ln k_{\infty}) \frac{2DKT_0}{c zB_{\infty} \cos \omega} \quad (34)
\]

we can write our result in the final form

\[
W = \frac{z^2}{1 + z + \frac{z^2}{2} + \frac{n^2(1 + z)}{2D}} \quad (35)
\]

This formula brings out the dependence of \( k \) on concentration which does not depend on the valency of the \( B \) ion nor on the nature of the other ions contributing to the ionic atmosphere. Then in any case the relationship between \( W \) and \( z \) should be the same.

For the dielectric dependence of the rate constant, Amis and Jaffe have introduced as a point of reference the point at which kappa equals zero as being the limiting case in which all electrostatic actions have disappeared. The equation (32) then will express the complete dependence of \( k \) on dielectric constant as on concentration.

Again they introduce dimensionless variables. They set

\[
k^2 = \frac{\lambda^2}{D}
\]

which gives for lambda the dimension cm\(^{-1}\) but free from D.
Setting then

\[ \lambda = \lambda a = \lambda r_0 \]  

(36)

and

\[ w' = (\ln k - \ln k_{k=0}) \frac{2}{{\varepsilon} z B u_0} \frac{2 KT}{\lambda^2 \cos \gamma} \]  

(37)

the general relation obtained is then

\[ w' = \frac{1}{D^2} \frac{1}{1 + \frac{5}{D} \frac{\lambda^2}{2D}} \]  

(38)

It should be noticed that \( z^2 \) and \( \lambda^2 \) are by their definitions proportional to the ionic strength.

The second part of this paper is devoted to the explanation of the alkaline decomposition of diacetone alcohol using the data published by Åkerlöf (2) (3) (4) for the reaction.

This reaction is that of an hydroxide ion reaction with a dipolar molecule as shown below:

\[
\begin{align*}
\text{CH}_3 & \quad \text{OH}^- \\
\text{CH}_3 - \text{C} - \text{CH}_3 & \quad \text{OH}^- \\
\text{CH}_3 & \quad 2 \text{CH}_3 - \text{C} - \text{CH}_3
\end{align*}
\]

By use of the equation of Amis and Jaffe (52) for reactions between ions and molecules this reaction may now be explained on the basis of the electrostatic theory for ion-dipoles in the cases where these electrostatic forces are predominant in determining the reaction velocity.
This reaction is particularly important since it is the first reaction to be investigated from the standpoint of the Amis and Jaffé theory which involves the reaction between a negative ion and a dipole molecule. In the original paper (7) good agreement was shown to exist between the kinetics of a positive ion and a dipole and the same agreement is shown to exist in this case of a negative ion reacting with a dipole.

Åkerlóf (2) (3) (4) has studied the decomposition of diacetone alcohol in alkaline hydroxide solutions containing variable concentrations of a variety of salts and in various mixed solvents differing widely in composition and dielectric constant. He has explained the observed kinetics of the reaction on the basis of changed activity of alkali in these various salt solutions and mixed solvents. The fluorides, carbonates, and sulfate salt solutions were observed to be anomalous in their effects upon the kinetics of the diacetone alcohol-hydroxide ion reaction. The mixed solvents isopropyl alcohol-water and methyl alcohol-n-propyl alcohol were also anomalous in their behavior. The equation of Amis and Jaffé (32) permits the study of the effects of neutral salts and of variable dielectric constant of the solvent upon the reaction between an ion and a dipolar molecule insofar as the effects are due to electrostatic forces. The diacetone alcohol-hydroxide ion reaction in the salt solutions and in the solvents of variable dielectric constant should fall in the scope
of this theory as long as effects other than those arising from electrostatics do not predominate.

In Tables VI-A, B, and C are given Åkerlöff's data for the decomposition of diacetone alcohol in potassium hydroxide potassium salts, sodium-hydroxide-sodium salts, and various alkaline hydroxides without the presence of salts. The constants specified in Tables VI-A and VI-B are pseudo-uni-molecular rate constants while both the pseudo-uni-molecular and the true bimolecular constants are given in VI-C. These constants are all calculated using time in minutes. In Fig. 7, these data are plotted against the critical curve represented by equation (35) of Amis and Jaffe. The sub-number for a circle represents the number of data for uni-univalent salts at a given y of which the circle is the mean position. The data for the pure alkaline hydroxides are plotted with symbols other than circles as indicated in the legend of Fig. 7. The kinetic rate in the presence of the uni-bivalent potassium and sodium chromates fall on a common curve represented by symbol circled-dot.

The data for the salt solutions, while not conforming exactly to the curvature of the theoretical line, do have the expected direction of change and the mean positions represented by the data fall fairly closely to the theoretical curve especially in the more dilute regions. This is the region where best agreement would be expected.
The data for the pure alkali hydroxides fit the curve only for regions of concentration up to a value of $\mu$ equal to 0.6. Even this is far beyond the range of concentration at which ion-ion reactions agree with the prediction of theory, since in these cases the agreement ordinarily conforms to theory only up to a value of $\mu$ somewhat less than 0.01. In Table VII are recorded the constants used in fitting Åkerlöf's data to the theoretical curve of Fig. 7. The value of these constants agree reasonably well with those found by Amis and Jaffe (7) for the inversion sucrose by hydrochloric acid.

In the case of the fluorides, carbonates, and sulfates the change of rate with concentration is opposite to that predicted by theory and hence there must be other than electrostatic forces involved when the rate constants of this reaction are measured in solutions of these salts. This anomalous behavior is in agreement with the observations of Åkerlöf.

Table VIII contains Åkerlöf's data (4) for the decomposition of diacetone alcohol in various mixed solvents when the concentration of sodium hydroxide is 0.1 N. Included in the table are the dielectric constants of the various solvents also taken from the data of Åkerlöf (1). The constants in this table are pseudo-unimolecular and the time is in minutes. Åkerlöf observed that in most cases the rate constant decreases with decreasing dielectric constant of the solvent, the decrease becoming progressively
less as the dielectric constant was continually lowered and in some cases the plot of the rate against the dielectric constant showed an inflection. In the case of isopropyl alcohol-water and methyl alcohol-n-propyl alcohol the rates increased with decreasing dielectric constant of the solvent. Åkerlöf noted that the effects in the various mixed solvents was opposite to that of acid hydrolysis of organic molecules such as esters. This, he thought, was surprising. Again the theory for ion-dipole reactions should account for the effects of the dielectric constant of the solvent observed upon the kinetics of the alkali-hydroxide-diacetone alcohol reaction, provided that these effects are dependent upon electrostatics. In Fig. 8 we have plotted the data on a curve represented by the requirements of the theory for rates of reaction between ions and dipole molecules as given by equation (38). On this curve we are unable to plot the data for isopropyl alcohol and methyl alcohol-n-propyl alcohol since the direction of the change of the velocity constant of the reaction with decreasing dielectric of the solvent is opposite to that predicted by theory. The other mixed solvents agree in direction and curvature fairly well over the range of dielectric constant from 50 to 78.5. This is the range found to agree with theory in the case of ion-ion reactions.

In Table IX the constants used in plotting these data are recorded. It can be seen from this table that
only ethyl alcohol and n-propyl alcohol give the expected values of the constants employed. For the other solvents the large values of the enhanced moment $\mu^*$ and of the square of the refractive index indicate a chemical effect which is in the same direction as the expected electrostatic effect. The result is a magnification of the contribution expected from electrostatics. Since the rate decreases with decreasing sodium hydroxide concentration and since theory predicts the decrease with a decrease in the dielectric constant of the solvent, then any chemical reaction which would decrease the effective concentration of hydroxide ion would add to the expected electrostatic effect. It is known that glycerine neutralizes sodium hydroxide to a marked extent (5). It is reasonable to suppose that ethylene glycol being similar in nature to glycerine will likewise effectively reduce the concentration of the hydroxide ion. Hence, with increasing amount of glycerol or glycol and a corresponding decrease of dielectric constant, a larger decrease of the rate constant than that predicted by electrostatics will be observed. This was found to be the case in the fading of brom phenol blue by sodium hydroxide when glycerine was used as one component of the solvent. (5) This would explain the unexpected decrease in the rate constants observed in the diacetone alcohol-hydroxide reaction in glycerol-water and glycol-water solvents. We are unable to explain the
very large effect of methyl alcohol upon the rate constants although Åkerlöf assumes that probably the sodium alcoholate is formed. Our experience with alcohol as a solvent would lead us to doubt this explanation as being the true cause of the observed result, since alkaline fading of various phthalein dyes in alcohol-water solvents conforms to the predictions of electrostatics. (8)

It does not seem logical to explain the deviations occurring in methyl alcohol on this basis of alcoholate formation when ethyl alcohol and isopropyl alcohol conform closely to the predictions of theory.
### TABLE VI-A

Data of Akerlof on Decomposition of Diacetone Alcohol in Potassium Hydroxide Potassium Salt Solutions

Decomposition in 0.1 N. KOH with added Potassium Salts

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<th>CrO₄²⁻</th>
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**TABLE VI-B**

Data of Akerlof on Decomposition of
Diacetone Alcohol in Sodium Hydroxide-
Sodium Salt Solutions

Decomposition in 0.1 N NaOH with added sodium salts

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**TABLE VII**

Constants used in Plotting Curves for Concentration

Effect in Fig. 7

\[ r_0 = 3 \text{ A}^\circ \text{ for uni-univalent compounds} \]
\[ r_0 = 5 \text{ A}^\circ \text{ for uni-bivalent compounds} \]

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TABLE VIII

Data of Akerlof on Decomposition of Diacetone Alcohol
by Sodium Hydroxide in Water Mixtures of Organic Solvents

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<td>23.8</td>
<td>64.0</td>
<td>30.3</td>
<td>65.2</td>
<td>46.0</td>
<td>54.9</td>
<td>187</td>
</tr>
<tr>
<td>60</td>
<td>16.2</td>
<td>60.0</td>
<td>21.6</td>
<td>59.4</td>
<td>38.4</td>
<td>50.1</td>
<td>182</td>
</tr>
<tr>
<td>70</td>
<td>10.9</td>
<td>55.6</td>
<td>15.8</td>
<td>54.7</td>
<td>28.7</td>
<td>45.0</td>
<td>182</td>
</tr>
<tr>
<td>80</td>
<td>50.6</td>
<td>13.2</td>
<td>49.3</td>
<td>21.6</td>
<td>40.1</td>
<td>188</td>
<td>32.8</td>
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<tr>
<td>90</td>
<td>45.5</td>
<td>43.7</td>
<td>15.4</td>
<td>35.7</td>
<td>196</td>
<td>28.1</td>
<td>270</td>
</tr>
<tr>
<td>99</td>
<td>40.1</td>
<td>37.7</td>
<td>10.3</td>
<td>31.5</td>
<td>231</td>
<td>24.3</td>
<td>500</td>
</tr>
</tbody>
</table>

5
TABLE IX

Constants Used in Plotting Curves in
Fig. 8

\[
\begin{align*}
\rho_0 &= 3 \, \text{A}^0 \\
\mu_0 &= 4 \times 10^{-18}
\end{align*}
\]

Substances used as solvents (NaOH = 0.1 N)

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \mu^* \times 10^{18} )</th>
<th>( n^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycerine</td>
<td>376</td>
<td>187</td>
</tr>
<tr>
<td>glycol</td>
<td>172</td>
<td>85</td>
</tr>
<tr>
<td>methanol</td>
<td>104</td>
<td>51</td>
</tr>
<tr>
<td>ethanol</td>
<td>6.61</td>
<td>2.31</td>
</tr>
<tr>
<td>N-propanol</td>
<td>15.66</td>
<td>5.83</td>
</tr>
</tbody>
</table>
Fig. 7

- Average of added salt rate constants
- NaOH
- LiOH
- KOH
- K\textsubscript{2}CrO\textsubscript{4}
- (NaOH-Na\textsubscript{2}CrO\textsubscript{4}
Fig. 8

- Glycerine
- Glycol
- CH\_3OH
- C\_2H\_5OH
- n-C\_3H\_7OH
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VITA

Ralph Theodore Overman was born Aug. 9, 1919 in Clifton, Arizona. He received the A. B. degree from Kansas State Teacher's College in Pittsburg, Kansas in 1939 and the M. S. degree in 1940 from the same institution. He was a Teaching Assistant during 1939-1940 in the Kansas State Teacher's College and entered the Graduate School of Louisiana State University in September, 1940. He was a Teaching Assistant in the Chemistry Department from September, 1940 until June, 1942 when he was employed by the Flintkote Company in New Orleans, La. as plant chemist. He returned as an Assistant in the department of Chemistry in October, 1942 which position he holds at the present time. He is now a candidate for the degree of Doctor of Philosophy.
Candidate: Ralph Theodore Overman

Major Field: Chemistry

Title of Thesis: The Kinetics and Mechanism of the Alkaline Fading of Iodo Phenol Blue. The Diacetone Alcohol-Hydroxide Ion Reaction

Approved:

Edward A. Ames
Major Professor and Chairman

Dean of the Graduate School

Examining Committee:

Date of Examination: