

AN ABSTRACT OF THE THESIS OF

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Abstract approved

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The kinetics of the iodine-formate reaction were studied spectrophotometrically in eight DMSO-water mixtures, including water and DMSO. In all cases, the reaction follows the stoichiometric equation, $I_3^- + HCOO^- \rightarrow CO_2 + 3I^- + H^+$. The rate law, $rate = k[\Sigma I_2][HCOO^-][I^-]^{-1}$, is observed in all solvent mixtures, provided that the $[I^-]$ is kept high compared to K_d , the dissociation constant of I_3^- . The value for this rate constant, k , varies from $2.4 \times 10^{-5} \text{ sec.}^{-1}$ in water to $5.0 \times 10^{-1} \text{ sec.}^{-1}$ in DMSO at 20.7°C , if ionic strength is 0.30. Log k is nearly a linear function of the mole fraction of DMSO.

The reaction rate is lowered by the presence of metal cations. This effect becomes more pronounced as the DMSO content of the solvent increases, and as the charge to size ratio of the cation increases and is attributed to the formation of ion-pairs. Approximate value for the dissociation constants for the K^+HCOO^- , Na^+HCOO^- ,

Li^+HCOO^- , and $\text{Ba}^{2+}\text{HCOO}^-$ ion-pairs were calculated from this cation effect with the assumption that the ion-pairs are unreactive.

$\Delta H^\ddagger$ and $\Delta S^\ddagger$ decrease about 4 kcal/mole and 8 entropy units respectively as the solvent changes from 40 to 80 mole per-cent DMSO.

The large effect of solvent upon the reaction rate, the specific cation effect, and the solvent effect upon the enthalpy and entropy of activation can all be attributed to specific solvation effects. The formate ion is solvated to a greater degree by water than by DMSO, due to the hydrogen bonding ability of water.

Kinetic isotope effect studies involving the formate hydrogen were made. The $k_{\text{H}}/k_{\text{D}}$ values varied from 2.1 in DMSO to 3.8 in water.

The following mechanism is consistent with our results. The rapid equilibrium, $\text{I}_3^- \rightleftharpoons \text{I}_2 + \text{I}^-$, is followed by the slow, rate determining attack of the I_2 molecules on the formate ion, $\text{I}_2 + \text{HCOO}^- \rightarrow \text{HCOOI}_2^-$. This latter species rapidly decomposes into the final products in a series of steps. The desolvation of the formate ion by increasing the DMSO content of the solvent facilitates the attack of the iodine molecule. The $k_{\text{H}}/k_{\text{D}}$ values indicate that the attack of the iodine molecule on the oxygen atoms results in a weakening of the carbon to hydrogen bond. The formate hydrogen is then more susceptible to removal by the solvent molecules.

Approximate values for the dissociation constant of the triiodide ion were determined potentiometrically. This constant decreases in value from about 1.2×10^{-3} in water to about 1×10^{-5} in 40 mole percent DMSO. Above 40 mole percent DMSO it remains in the range of $(0.4 - 1.0) \times 10^{-5}$.

A STUDY OF THE IODINE-FORMATE REACTION
IN DIMETHYLSULFOXIDE-WATER MIXTURES

by

FREDERICK WAYNE HILLER

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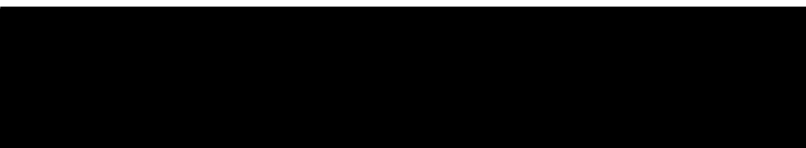
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A STUDY OF THE IODINE-FORMATE REACTION IN DIMETHYLSULFOXIDE-WATER MIXTURES

INTRODUCTION

Solvent Effects

During the last ten years there has been a considerable increase in interest in the effect of the solvent upon chemical change. There have been many investigations, especially in the field of organic chemistry, in which changing the solvent either changed radically the rate of a given reaction, or else changed the course of that reaction. Much interest has been centered upon the differences between protic solvents, such as water, methanol or ethanol, and dipolar, aprotic solvents, such as dimethylsulfoxide (DMSO), dimethylformamide (DMF) and dimethylacetamide (DMA).

The most obvious solvent effect is that due to the dielectric constant for the medium, since the dielectric constant represents the degree of shielding between charged particles due to the presence of the solvent. Scatchard (66) gives a well known formula, which relates the rate constant for a reaction involving ions to the dielectric constant of the medium. This equation predicts that the logarithm of the rate constant should vary linearly with the reciprocal of the dielectric constant. The slope of this line is dependent upon the charges on the reacting ions and the radius of the activated

complex. Similar equations have been derived for the cases of dipole-dipole (52, 63) and of ion-dipole (52, 63) reactions. The later equation predicts that the rate for an ion-dipole reaction should be slightly greater in a medium of lower dielectric constant.

The second principle effect of the solvent is due to its ability to solvate the reacting ions or molecules. In general, protic solvents, have the ability to form hydrogen bonds with small anions, while aprotic solvents do not (42, 46, 56, 57, 59). Solvation of cations depends primarily upon the solvent's dipole moment and the availability of electrons for coordination to the cation.

There have been at least two linear free energy relations devoted to the empirical correlation of the influence of the solvent on the rate of a given type of chemical reaction. One of these is that due to Winstein and co-workers (22-25, 63, 69, 79, 80), in which the rate of solvolysis reactions is related to the solvent by the equation $\log (k/k_o) = mY$. The Y 's are factors dependent on the solvent and the m 's are factors dependent on the substance solvolyzed. Y has the value zero in the standard solvent, 80% ethanol in water. The standard substrate is usually *t*-butyl chloride. Values of Y were determined for a wide range of solvents. The solvent factor, Y , is considered a better measure of the ionizing ability for that solvent than is the dielectric constant.

Kosower (47-49) set up an empirical factor, related to solvent

polarity, called a "Z" factor based on the shifting of the charge-transfer band of 1-ethyl-4-carbomethoxypyridinium iodide by the various solvents and solvent mixtures. He then proceeded to correlate this factor with some kinetic data, including iodide exchange between alkali metal iodides and methyl iodide and the reaction of amines with alkyl halides (49).

Cavell (6) studied the rate of reaction of sodium iodide with n-butyl bromide in acetone-water mixtures. Cavell and Speed studied the rate of iodide exchange between sodium iodide and n-butyl iodide in acetone-water (7) and in acetonitrile-methanol (8) mixtures. They concluded that their results could not be explained on the basis of dielectric constant alone, but that in addition, there was a specific interaction between the protic component of the solvent mixture, i. e. , water or methanol, and the iodide ion. The interaction was shown to be due to hydrogen bonding between the protic solvent and the iodide ion, forming a species which reacted slower than the free iodide ion.

Miller and Parker (56) studied bimolecular nucleophilic substitution reactions in numerous solvents, both protic and aprotic. They found the reaction rates to be approximately 10^5 times as fast in dipolar, aprotic solvents as in protic solvents. It was concluded that the reaction rate is largely dependent upon the degree of solvation of the substituting anion. This solvation is affected by (1) the

dipole moment of the solvent, (2) the amount of shielding of the dipole charges, and (3) the nature of the atoms carrying the dipole charges. In general, small anions are solvated more by protic solvents due to hydrogen bonding, while large, bulky anions are solvated more by dipolar, aprotic solvents, like DMSO and DMF.

Parker (10, 11, 56-60) has done considerable work on the effects of solvation by aprotic and protic solvents and has written a review article (59) on aprotic solvation. Some of his work, other than the solvent effect on kinetics of nucleophilic displacement, includes solvation effects on spectra (60), effects of solvation on acid dissociation constants (10), and determination of solvent activity coefficients for iodide ion in methanol as compared to dimethylformamide (58). In the latter case, he divides the solvent activity coefficient into two parts, one due to hydrogen bonding effects and one due to other solvent effects. The hydrogen bonding activity coefficient, of course, applies only in methanol.

Much work has been done on nucleophilic substitution reactions in aprotic solvents. Parker and co-workers (11, 56, 57) have contributed much from the point of view on anion solvation. Berge and Uglestad (3) have noted that cation solvation is important in nucleophilic substitution reactions involving sodium or potassium phenoxide. The activation energy for the displacement of bromide ion with azide ion in butyl bromide was correlated with the basicity of the

solvent by Delpuech (15). The chemical shift of the hydrogen in CHCl_3 was taken as a measure of the basicity. Dipolar aprotic solvents were more basic in this sense than were protic solvents. The most effective solvent for accelerating this reaction was hexamethylphosphoramide.

Addison, Sheldon and Hodge (1) as well as Straub, Sisler, and Ryschkewitch (71) studied the effect of various solvents upon the reaction of nitrogen tetroxide with numerous metals. They concluded that this reaction rate depended upon (a) the ionizing power of the solvent, (b) the donor properties of the solvent toward nitrogen tetroxide and (c) the coordinating ability of the solvent toward the metal ion.

Studies in Dimethylsulfoxide-Water Mixtures

The solvent mixture, dimethylsulfoxide and water, is an attractive one in which to study the effect of variation in solvent upon chemical change. Both liquids are characterized by having a fairly high dielectric constant, 48.9 for dimethylsulfoxide (59, 67, 81) as compared to 78 for water. Both are associated liquids (59, 67, 81). Both are good solvents (39, 59, 67) for many salts, although salts of large polarizable anions are more soluble in DMSO than those of small anions (59). Many salts are completely ionized in DMSO (68). However, water is a typical protic solvent and can form hydrogen

bonds in which it donates the hydrogen, but dimethylsulfoxide, a typical dipolar, aprotic solvent, can not (59, 61).

Nuclear magnetic resonance studies (20), heat of mixing studies (12, 20, 41), measurements of dielectric constant (18, 53, 67), viscosity measurements (12, 54, 67), and thermodynamic excess functions (40) on dimethylsulfoxide-water mixtures indicate that there is a great deal of association between the molecules of the two solvents.

Wolford (81), in his study of the acid catalyzed hydrolysis of acetal in DMSO-water mixtures, considers three regions of solvent composition. These are (1) less than 30 mole percent DMSO in which the association is primarily between water molecules, (2) between 30 and 50 mole percent DMSO, where the degree of association between the dimethylsulfoxide and the water molecules is the greatest and (3) above 50 mole percent, where the properties approach those of the aprotic DMSO. In the 30-40 mole percent DMSO range, most of the physical properties show their greatest deviation from the mean of their values in DMSO and water.

Tommila and co-workers have made several studies involving dimethylsulfoxide-water mixtures (34, 73-76). In the solvolysis of benzyl chloride (76), they found that logarithm of rate constant was a linear function of the water concentration. In the alkaline hydrolysis of benzoic acid esters (75) and of ethyl acetate (73) the rate of

solvolysis increased with dimethylsulfoxide concentration. This effect becomes noticeably great at about 70 volume percent dimethylsulfoxide. The cause of the rapid increase in basic hydrolysis was attributed to the desolvation of hydroxide ions as the percent dimethylsulfoxide increased. In the acid hydrolysis of ethyl acetate (74), there was a maximum rate at about 70 volume percent water. They also found that the extent of olefin formation from tertiary-butyl halides (34) was proportional to the concentration of DMSO.

Roberts (64, 65) and Hojo, Utake and Yoshido (35) were also interested in ester saponification rates in DMSO-water mixtures and agree that the enhancement of the reaction as the concentration of dimethylsulfoxide increases is due to desolvation of the hydroxide ion.

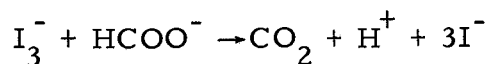
Krueger (50) has shown that the oxidation of iodide ion by dimethylsulfoxide in DMSO-water mixtures was strongly dependent upon the solvent composition as well as being catalyzed by the halide ions acting as nucleophiles. Chlorides were better catalysts than bromides at the higher concentrations of dimethylsulfoxide. This is probably due to the greater desolvation of the smaller chloride ion as water molecules are being replaced with dimethylsulfoxide molecules.

The preceding has been a discussion of only some of the more important work done on solvent effects. The emphasis has been on

studies involving dimethylsulfoxide and water, since that is the solvent system used in our investigation of the iodine-formate reaction. Most of the previous work has been in the field of organic chemistry. Only relatively few studies have been on inorganic reactions.

The Iodine-Formate Reaction

In order to extend the study of the solvent effects into the field of inorganic chemistry, the study of the oxidation of formate ion by iodine in DMSO-water mixtures was chosen. This reaction has been well investigated in water (4, 9, 16, 17, 33, 43, 51) and follows the following stoichiometric equation



It is of interest to determine what effect changing the solvent from water to the aprotic DMSO has upon the kinetics of this reaction.

The feasibility of studying this reaction in DMSO-water mixtures would depend upon several factors, including the solubility of the reactants and the extent to which they interact with the dimethylsulfoxide. Iodine, iodides and formates are fairly soluble in dimethylsulfoxide-water mixtures. Even though iodides are oxidized by dimethylsulfoxide (52) this reaction is slow, unless the acidity is high. Iodine forms a 1-1 complex with DMSO (19, 30, 44).

This complex is, however, not as stable as triiodide ion in these solvent mixtures. It is, then, possible to study this reaction in the presence of DMSO.

Dhar (16) first studied the reaction of formic acid with iodine in aqueous sodium acetate solution. He noted that the reaction rate was proportional to the iodine and formic acid concentrations, but that the rate decreased as the concentration of iodide ion increased. He called this a case of negative catalysis by the iodide.

Hammick and Zvegintzov (33) studied the kinetics of the reaction of iodine with formic acid at 60°C. They observed that the reaction rate was inversely proportional to the acid concentration and concluded that the rate was dependent upon formate ion concentration, but not on that of formic acid molecules. They noted the inverse dependence upon iodide ion concentration and assumed a rate law of the form,

$$\frac{-d[\Sigma I_2]}{dt} = \frac{k_1 [HCOO^-] [\Sigma I_2]}{1 + [I^-]/K_d}$$

where K_d is the dissociation constant for the triiodide ion. This rate law was analogous to that found previously for the bromine-formic acid reaction by Hammick, Hutchinson and Snell (32). K_d for triiodide ion has been measured by several different procedures (2, 13, 14, 36, 37, 62) and is about 1.4×10^{-3} at 25°C. Thus, if

the concentration of the iodide ion is left reasonably high, $[I^-]/K_d$ is large compared to unity and the rate law reduces to:

$$\text{Rate} = \frac{k[\text{HCOO}^-][\Sigma I_2]}{[I^-]}$$

In this rate law, k is the product of k_1 and K_d , and $[\Sigma I_2]$ represents the total iodine concentration present in the form of I_2 and I_3^- .

Chow (9) repeated some of the kinetic studies in his work relating oxidation potentials to kinetics. He verified the involvement of the triiodide equilibrium and the dependence on the formate ion as opposed to formic acid. More recently, Kunaszewska and Jozefowicz (51) extended the work to low iodide and formate ion concentrations.

The object of this investigation is to determine what effect changing the solvent from water to DMSO has upon the reaction between iodine and formate ions. Among the reasons for choosing this reaction for our study are: (1) it has been well studied in water, (2) it will take place in DMSO-water mixtures, without important side reactions with the DMSO, (3) it is oxidation-reduction, while most other investigations have been displacement, (4) it has a convenient rate, and (5) the reactants all have sufficient solubility in all solvent mixtures to allow reactions to occur in a homogeneous

system. This particular solvent mixture was chosen because it represents the changing from a typical protic solvent, to a typical aprotic solvent of fairly high dipole moment.

Some questions that might be answered by this study are: Is the change in rate due only to the change in dielectric constant of the medium or are solvation effects involved also? Is the mechanism of the reaction affected by the solvent change? Are there any specific cation effects? How does changing the solvent affect the activation energy and the entropy of activation for this reaction?

EXPERIMENTAL

Procedures and Equipment

The reaction of iodine with formate ion was followed by measuring the disappearance of free iodine as the reaction proceeded. This was accomplished by taking repeated measurements of the absorbancy of the reaction mixture at the wave length of 380 millimicrons or some other wave length near the absorption peak of the triiodide ion found at 353 millimicrons in water. In dimethylsulfoxide-water mixtures this absorption peak is around 365 millimicrons. Preliminary experiments indicated that any wave length near this peak would serve to indicate the decrease in iodine concentration with time. Beer's Law plots indicate that the absorbancy at wave lengths near this peak is a good measure of the iodine content.

A Beckman, Model DU spectrophotometer was used to make these measurements. This instrument was equipped with a new Beckman DU power supply, which operates from line voltage. The detector was a photomultiplier.

The cell compartment was thermostated by means of water cooled temperature baffles. Cooling water for these was supplied by a constant temperature bath controlled by a Beckmann type

thermoregulator. Temperature variations in the cell compartment were thus controllable to within 0.1°C . The main cause of the deviation was due to large variations in the room temperature.

The temperature in the cell compartment itself was measured by a thermistor. This in turn was calibrated against a 50°C thermometer which had previously been calibrated by the National Bureau of Standards.

For each run two solutions were prepared and placed in 50 milliliter glass stoppered Erlenmeyer flasks. One of the solutions contained the formate ion and the other contained the iodine and some of the iodide ion required in the sample. Either or both solutions contained iodides and perchlorates, depending on the requirements for that particular run. Before the run these flasks were kept in a water bath, the temperature of which was approximately that of the run.

In order to stabilize and maintain the temperature in the spectrophotometer cell compartment before the run, water was pumped continuously from the constant temperature bath through the cooling baffles about the cell compartment and back to the water bath. It was necessary to start this process at least one to two hours before the start of the run. It was also necessary to turn on the power for the tungsten lamp source for a period of at least an hour ahead of time so that temperature equilibrium could be reached

in the cell compartment before the run began. The cells and the blank to be used were also placed in the cell compartment about half an hour before the initiation of a given run. After the cell compartment temperature was stabilized, the spectrophotometer was made ready for operation and allowed to warm up for 10 to 15 minutes.

The run was then started by first mixing the solutions in the two flasks rapidly and reading the time on an electric timer. After the solutions were thoroughly mixed, a sample of the mixture was transferred to the cell in the cell compartment by means of a medicine dropper. Then an initial absorbancy reading was taken. In this manner an initial reading was usually obtained 50 to 60 seconds after the solutions were mixed. Thereafter, absorbancy and time readings were normally taken at intervals chosen such that the decrease in absorbancy between reading was approximately 10% of the previous reading. Usually 20 to 25 such readings were taken. A reading was also taken after about ten half-lives. This was considered to be the absorbancy after infinite time or an infinity reading.

In order to determine the rate constant, the differences between the absorbancy and the infinity reading was plotted against time on semilog paper. The points were normally found to lie on a straight line, indicating the reaction was first order in iodine. The rate constant was calculated from the slope of this line in a manner which will be described later.

The Solvent

The original dimethylsulfoxide was obtained from Crown Zellerbach. This was pretreated by adding 10-12 pellets of potassium hydroxide to approximately 1700 milliliters of DMSO. This mixture was then heated, with constant stirring, until the pellets dissolved and the DMSO took on a yellow coloration. The DMSO was then distilled twice under a pressure of 8-10 mm Hg through 16-inch distilling columns filled with glass helices. The distillation temperature varied from 70 to 80°C depending on the pressure available from the aspirator. The pretreatment with potassium hydroxide was found necessary to remove small amounts of a reducing impurity found in the dimethylsulfoxide. This impurity could not be removed by simply doubly distilling. Karl Fischer titrations on doubly distilled DMSO have shown the water content to be 0.02% or less by weight.

The solvent used in the various runs consisted of a mixture containing dimethylsulfoxide, treated as indicated above, and the appropriate amount of distilled water. In most cases the distilled water had previously been redistilled from basic permanganate.

The procedure used in making up the solvent mixture consisted of (a) weighing the dimethylsulfoxide, (b) calculating the amount of water required to give a solvent mixture of the correct

composition and then (c) slowly adding this amount of water to the partially frozen dimethylsulfoxide by means of a buret.

Reagents

The iodine used in this study was Baker's resublimed iodine. It was used directly as obtained.

Reagent grade potassium and sodium iodides were recrystallized from water and dried in an evacuated desiccator over phosphorus pentoxide.

The sodium formate was Baker's reagent grade. The potassium formate was made by neutralizing some 88.5% reagent formic acid with potassium hydroxide solution, evaporating to dryness, and then recrystallizing from water. This product was then dried at 100°C in presence of phosphorus pentoxide in an evacuated chamber.

The potassium perchlorate was Baker's reagent grade and was used after drying. Reagent grade sodium perchlorate was recrystallized from water, then dried before use. The lithium and barium perchlorates were made by neutralizing the respective hydroxides with 60% perchloric acid and then evaporating the water. The products were recrystallized from water and then dried at 100°C over phosphorus pentoxide in an evacuated chamber.

Tetraethylammonium perchlorate and tetraethylammonium

iodide were obtained from Eastman Organic Chemicals. The iodide was twice recrystallized from water and then dried in an evacuated desiccator over phosphorus pentoxide.

An attempt was made to make tetraethylammonium formate by neutralizing formic acid with tetraethylammonium hydroxide. It was found that the salt could not be isolated from the solution without decomposition. The tetraethylammonium formate used was a solution produced by carefully neutralizing standardized 10% tetraethylammonium hydroxide with formic acid and then adding enough DMSO to give the correct solvent composition. The procedure was deemed satisfactory since the concentration of the formate ion could be calculated from the hydroxide concentration and since any excess formic acid molecules do not enter into the reaction.

Sodium deuterioformate, whose isotopic purity was 98%, was obtained from Merck, Sharp and Dohme of Canada, Limited. It was checked for basic impurities and analyzed for carbon and hydrogen content. The average result of this analysis was 2.8% deuterium and 17.5% carbon. This is in close agreement to the theoretical values of 2.9% deuterium and 17.4% in pure sodium deuterioformate.

All reagents except the iodine were stored in an evacuated desiccator over phosphorus pentoxide. The iodine can not be stored in this manner because of its high vapor pressure. Several

checks were made on the ability of the various perchlorates and iodides to reduce iodine under the experimental conditions, since such a reduction would interfere with the reaction studied. The only reagents which proved troublesome in this respect were sodium iodide and sodium perchlorate. These had to be recrystallized from water frequently.

Preliminary Tests

At first, the reaction was studied in 75% dimethylsulfoxide by weight. It was shown that the rate law was the same as has been previously been found to be the case in water by Hammick and Zvegintzov (33). That is, the reaction is first order in total free iodine, first order in formate ion and inversely proportional to iodide ion concentration (equation 1).

$$(1) \quad \text{Rate} = \frac{k[\Sigma I_2][HCOO^-]}{[I^-]}$$

Most runs were made with the concentrations of both the formate and iodide ions in great excess compared to that of free iodine. Thus, the concentrations of these can be considered as remaining constant throughout the run.

Hammick and Zvegintzov (33) report that there is no dependence on formic acid molecules, i. e., that only formate ions are

oxidized by the iodine. The lack of formic acid dependence was demonstrated in 75% DMSO by making kinetic runs containing both sodium formate and formic acid but calculating the rate constant only on the basis of the formate ion concentration. The rate constant thus calculated did not vary with formic acid concentration.

The lack of a photosensitized reaction was demonstrated by running two identical samples simultaneously. One of these, however, was exposed to ultraviolet light at 365 millimicrons and a slit width of 2 millimeters as much as possible between readings. The other was exposed to light only during the reading itself at 450 millimicrons and a slit width of 0.035 millimeters. Both samples reacted at the same rate. Thus, a photosensitized reaction was discounted.

The literature (33) states that the stoichiometry of the reaction is as follows:



This stoichiometry was checked in 75% and 95% DMSO by allowing reaction mixtures to react completely, boiling gently to remove dissolved CO_2 and then titrating with standard sodium hydroxide, using a Beckman Model 72 pH meter to indicate the end point. The resulting data is found in Table 1. The above stoichiometry requires that the number of millimoles of H^+ produced be the same as the

number of millimoles of I_2 used.

Table 1. Results of Titration Data in Stoichiometry Check

Wt. %DMSO	Millimoles of Iodine	Millimoles of $HCOO^-$	Millimoles H^+ produced
75.00	0.066	0.78	0.062
75.00	0.066	0.78	0.062
75.00	0.066	0.78	0.062
75.00	0.059	0.33	0.057
75.00	0.059	0.33	0.057
75.00	0.059	0.33	0.059
95.00	0.046	excess	0.046
95.00	0.046	excess	0.047
95.00	0.046	excess	0.047

The $[H^+]/[I_2]$ ratio obtained tends to be somewhat lower than predicted by the stoichiometric equation. Possibly this is due to the removal of some of the acid as formic acid when the solution is boiled. Some samples titrated without boiling required too much base due to dissolved CO_2 produced in the reaction. The titration results indicate that the stoichiometry has not changed by adding DMSO.

Solvent Effect

The effect of changing the solvent upon the kinetics of the iodine-formate reaction was determined by making several measurements of the rate constant, k , at each of eight different solvent compositions, varying from water to DMSO. The rate constant was

measured for several samples at each solvent composition. These samples were chosen so that the concentrations of the formate and of the iodide ions had at least a twofold variation from sample to sample. The kinetic data for these runs are listed in Table 2 through 10 and summarized in Table 11.

All these runs were made with an ionic strength of 0.30 by adding necessary amounts of KClO_4 or NaClO_4 . Above 75.00% DMSO by weight, the only cation present is potassium ion. Below this solvent composition only sodium ions were present. The reason for this change is due to the low solubility of potassium perchlorate in solvent mixtures containing more than 25% water by weight.

The rate of disappearance of the iodine is proportional to the ratio of the concentrations of the formate to iodide ions. This ratio, as well as the solvent composition, determines the half-life of a given run.

In most cases the concentrations of the formate and of the iodide ions were high compared to that of free iodine. Therefore, the concentrations of these ions did not change significantly during the run. The first order dependence on total free iodine was then demonstrated by the fact that the normal first order plots, $\log$ absorbancy versus time, yielded a straight line. If one assumes the rate law given in Equation 1, the slope (S) of this line should be

$$(3) \quad S = \frac{k}{2.303} [\text{HCOO}^-][\text{I}^-]^{-1}$$

and k should be obtained by

$$(4) \quad k = 2.303 S [\text{I}^-][\text{HCOO}^-]^{-1}$$

The dependence of the rate on iodide and formate ions is then demonstrated by varying the concentrations of iodide and formate ions but obtaining the same value of k (within experimental error) when substituting in the above equation.

Table 2. Kinetic Data for All Sodium Ion Runs in Water at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^3 [\text{I}^-], \text{M}$	$10^2 [\text{HCOO}^-], \text{M}$	$10^5 k, \text{sec}^{-1}$
3.59	4.72	7.51	2.57
3.59	4.72	15.0	2.66
7.38	40.1	20.0	2.52
7.38	28.1	20.0	2.32
7.38	22.1	20.0	2.55
7.38	7.44	20.0	2.62
7.38	6.41	20.0	2.55
7.38	4.10	20.0	2.57
3.70	18.1	15.0	2.31
3.28	16.1	16.6	2.43
4.22	9.21	12.5	2.29
2.74	6.43	18.7	2.50
4.23	4.46	12.5	2.43
3.62	3.82	15.0	2.32
4.81	6.77	10.0	2.37
4.81	6.01	10.0	2.22
4.81	5.25	10.0	2.31
4.81	4.48	10.0	2.31
4.81	3.72	10.0	2.11

Ionic Strength = 0.300 ± 0.005

Average $k = 2.43 \times 10^{-5} \text{sec}^{-1}$

Standard Deviation = 0.13×10^{-5} or 5.3%

Table 3. Kinetic Data for All Sodium Ion Runs in 52.02% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^3 [I^-], M$	$10^2 [HCOO^-], M$	$10^4 k, \text{sec}^{-1}$
38.7	40.6	3.75	1.86
38.7	40.6	5.00	1.92
38.7	40.6	7.50	1.86
38.7	40.6	10.0	1.85
38.7	40.6	15.0	1.94
3.40	8.28	3.13	1.75
3.92	3.10	0.92	2.10
3.92	4.04	1.22	2.01
3.92	5.53	1.83	2.08
5.14	28.1	3.27	1.87
5.14	21.8	3.27	1.91
4.40	25.8	3.93	1.91
5.14	12.3	3.27	1.88
4.80	9.85	3.49	1.87
4.40	6.86	3.93	1.84
3.18	50.8	10.2	1.84
3.18	42.7	10.2	1.79
3.18	34.6	10.2	1.82
3.18	26.5	10.2	1.77
3.18	18.4	10.2	1.76
3.18	10.3	10.2	1.77

Ionic Strength = 0.300 ± 0.005 Average $k = 1.87 \times 10^{-4} \text{sec}^{-1}$ Standard Deviation = 0.09×10^{-4} or 5.1%

Table 4. Kinetic Data for All Sodium Ion Runs in 75.00% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^2 [HCOO^-], M$	$10^3 k, \text{sec}^{-1}$
2.11	10.0	6.13	2.15
4.37	20.0	4.00	2.10
4.37	17.6	4.00	2.07
4.37	15.2	4.00	2.02
4.37	12.8	4.00	2.10
4.37	10.4	4.00	2.05
4.37	7.98	4.00	2.02
3.18	8.07	3.38	1.90
3.08	8.00	3.98	1.97
3.08	8.00	3.98	2.04
3.08	8.00	3.98	2.00
3.08	8.00	3.98	2.05
3.08	8.00	3.98	2.27
3.08	8.00	3.98	2.16

Ionic Strength = 0.300 ± 0.005 Average $k = 2.06 \times 10^{-3} \text{sec}^{-1}$ Standard Deviation = 0.09×10^{-3} or 4.4%

Table 5. Kinetic Data for All Potassium Ion Runs in 75.00% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^2 [HCOO^-], M$	$10^3 k, \text{sec}^{-1}$
5.98	20.1	3.89	2.54
5.98	17.7	3.89	2.41
5.98	15.3	3.89	2.53
5.98	12.9	3.89	2.62
5.98	10.5	3.89	2.57
5.98	8.07	3.89	2.68
3.85	4.19	15.51	2.49
3.84	4.19	11.11	2.48
3.71	15.0	1.95	2.51
3.71	15.0	2.94	2.39
3.71	15.0	3.93	2.55
3.71	15.0	4.42	2.62
3.71	15.0	5.91	2.66
2.81	6.66	1.43	2.30
2.78	6.67	1.34	2.30
2.86	6.01	2.01	2.40
2.59	3.33	1.00	2.49

Ionic Strength = 0.300 ± 0.005 Average $k = 2.48 \times 10^{-3} \text{sec}^{-1}$ Standard Deviation = 0.12×10^{-3} or 4.9%

Table 6. Kinetic Data for All Potassium Ion Runs in 86.68% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$10^2 k, \text{sec}^{-1}$
5.30	28.2	20.1	1.59
3.35	27.5	26.8	1.63
5.30	19.4	6.70	1.59
5.30	21.6	10.0	1.59
5.30	23.8	13.4	1.62
4.39	12.8	5.10	1.63
4.39	10.5	5.10	1.55
4.39	9.02	5.10	1.54
4.79	8.20	4.64	1.61
4.39	6.02	5.10	1.63

Ionic Strength = 0.300 ± 0.005 Average $k = 1.60 \times 10^{-2} \text{sec}^{-1}$ Standard Deviation = 0.03×10^{-2} or 2.0%

Table 7. Kinetic Data for All Potassium Ion Runs in 91.01% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], m$	$10^2 k, \text{sec}^{-1}$
4.50	13.0	3.80	3.53
3.68	18.2	5.18	3.71
3.37	17.0	5.69	3.79
4.50	29.7	3.80	3.81
4.50	21.3	3.80	3.72
3.37	29.4	5.69	3.81
4.52	29.3	8.43	3.68
3.77	29.1	9.83	3.85
3.01	29.0	11.2	3.90
2.66	29.6	4.96	3.85
3.01	29.5	5.62	3.89

Ionic Strength = 0.300 ± 0.005 Average $k = 3.80 \times 10^{-2} \text{sec}^{-1}$ Standard Deviation = 0.08×10^{-2} or 2.0%

Table 8. Kinetic Data for All Potassium Ion Runs in 94.55% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$10^2 k, \text{sec}^{-1}$
2.89	29.8	2.73	7.99
3.85	29.7	3.64	7.95
3.49	29.2	8.19	8.06
2.89	29.4	6.83	8.18
2.89	29.1	9.56	8.45
3.61	9.93	1.60	8.01
3.16	12.4	2.00	8.07
2.71	14.8	2.40	8.57
3.61	30.0	1.60	8.36
3.16	29.9	2.00	8.30
2.70	29.8	2.40	8.31
2.20	10.0	1.93	7.85
2.21	6.65	4.12	8.42
2.53	6.02	.93	7.94
3.34	5.99	.99	8.05
3.42	15.7	4.20	7.98
3.13	14.6	4.62	8.16
4.04	29.7	2.61	7.87
3.68	5.99	1.06	8.12
3.10	7.35	1.01	7.78
3.66	10.3	0.996	7.99

Ionic Strength = 0.300 ± 0.005 Average $k = 8.12 \times 10^{-2} \text{sec}^{-1}$ Standard Deviation = 0.21×10^{-2} or 2.6%

Table 9. Kinetic Data for All Potassium Ion Runs in 97.50% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^3 [HCOO^-], M$	$10^1 k, \text{sec}^{-1}$
3.47	2.99	1.01	1.92
3.47	2.99	1.21	1.90
3.47	2.99	1.41	1.89
3.47	2.99	1.61	1.91
3.47	2.99	1.81	1.90
3.47	2.99	2.02	1.90
3.04	2.99	1.01	1.82
3.04	2.69	1.01	1.80
3.04	2.39	1.01	1.80
3.04	2.09	1.01	1.78
3.04	1.79	1.01	1.81
3.04	1.49	1.01	1.79

Ionic Strength = 0.300 ± 0.005 Average $k = 1.85 \times 10^{-1} \text{sec}^{-1}$ Standard Deviation = 0.05×10^{-1} or 3.0%

Table 10. Kinetic Data for All Potassium Ion Runs in 100% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^4 [HCOO^-], M$	$10^1 k, \text{sec}^{-1}$
4.32	2.50	12.9	5.28
4.32	2.50	7.7	5.05
3.37	2.99	6.29	5.06
3.37	2.99	7.55	5.00
3.37	2.99	8.81	5.07
3.37	2.99	10.1	4.90
3.37	2.99	11.3	4.91
3.37	2.99	12.6	4.80
3.12	2.99	5.37	4.84
3.12	2.69	5.37	4.77
3.12	2.40	5.37	4.78
3.12	2.10	5.37	5.16
3.12	1.80	5.37	5.07
3.12	1.50	5.37	4.98

Ionic Strength = 0.300 ± 0.005 Average $k = 4.98 \times 10^{-1} \text{sec}^{-1}$ Standard Deviation = 0.15×10^{-1} or 3.0%

Table 11. Summary of the Kinetic Results in Various Mole Fractions DMSO

Mole Fraction DMSO	% DMSO	Average Value of k	Cation Present
0.00	0.00	2.43×10^{-5}	Sodium
0.200	52.02	1.87×10^{-4}	Sodium
0.409	75.00	2.06×10^{-3}	Sodium
0.409	75.00	2.48×10^{-3}	Potassium
0.600	86.68	1.60×10^{-2}	Potassium
0.700	91.01	3.80×10^{-2}	Potassium
0.800	94.55	8.12×10^{-2}	Potassium
0.900	97.50	1.85×10^{-1}	Potassium
1.00	100	4.98×10^{-1}	Potassium

At low concentrations of DMSO, the formate to iodide concentration ratio has to be high so that two half lives can be observed in a reasonable time. This means that the concentration of iodide ion must be relatively low. When the concentration of iodide ion becomes comparable to the dissociation constant for triiodide ion (I_3^-), one must consider the effect of the formation of triiodide ion upon the reaction (33). The rate expression becomes

$$(5) \quad \text{Rate} = \frac{k_1 [\text{HCOO}^-] [\Sigma I_2]}{1 + [I^-]/K_d}.$$

Here, K_d is the dissociation constant of triiodide ion. The rate

constant, k_1 , in this expression is related to the rate constant, k , of Equation (1) by the expression,

$$(6) \quad k = k_1 K_d.$$

In all runs except those in water, the concentration of iodide ion is much greater than K_d and this equation reduces to the one given in Equation (1).

In water, however, it is necessary to make the amount of iodide ion present as small as feasible. In order to have reactions fast enough so that two half lives could be observed in three hours time, it was necessary to have the iodide concentration in the same order of magnitude as K_d but still much greater than the concentration of free iodine. As a consequence of the small iodide concentrations in water, the value for the rate constant, calculated on the basis of Equation (4), was corrected by the factor,

$$1 + K_d/[I^-].$$

At high concentrations of dimethylsulfoxide the formate to iodide concentration ratio had to be relatively low. This means that the concentration of the formate ion was, in some cases, less than 30 times that of free iodine. In these cases, the assumption that for all practical purposes the concentration of the formate ion does not change during the run is no longer valid. When the formate

to iodine concentration ratio was less than 30, the function $\log [1 + (a-1)(A_0/A)]$ was plotted against time, where A_0 and A are the absorbancies at time zero and time t , respectively, and a is the original ratio of the concentration of formate ion to that of free iodine. The slope (S) of this line is $\frac{bk}{2.303}$ where b is the product of $(a-1)$ with the original concentration of free iodine and k is the rate constant. One then obtains the value for k by:

$$(7) \quad k = \frac{2.303 S[I^-]}{F_{oo} - I_{oo}},$$

where $F_{oo} - I_{oo}$ is the difference between the original concentration of formate ion and that of free iodine. See Appendix I for the derivation of this formula.

This type of plot yielded better straight lines for runs of low formate ion concentrations than did the normal, log of absorbancy versus time, graph. In general the rate constants thus obtained were slightly higher in value than those obtained normally for the same run.

The effect of the solvent composition upon the rate constant for this reaction is shown graphically in Figure 1. One should note the almost straightness of the upper and lower portion of this curve, and that the rate of this reaction is increased by about 10^4

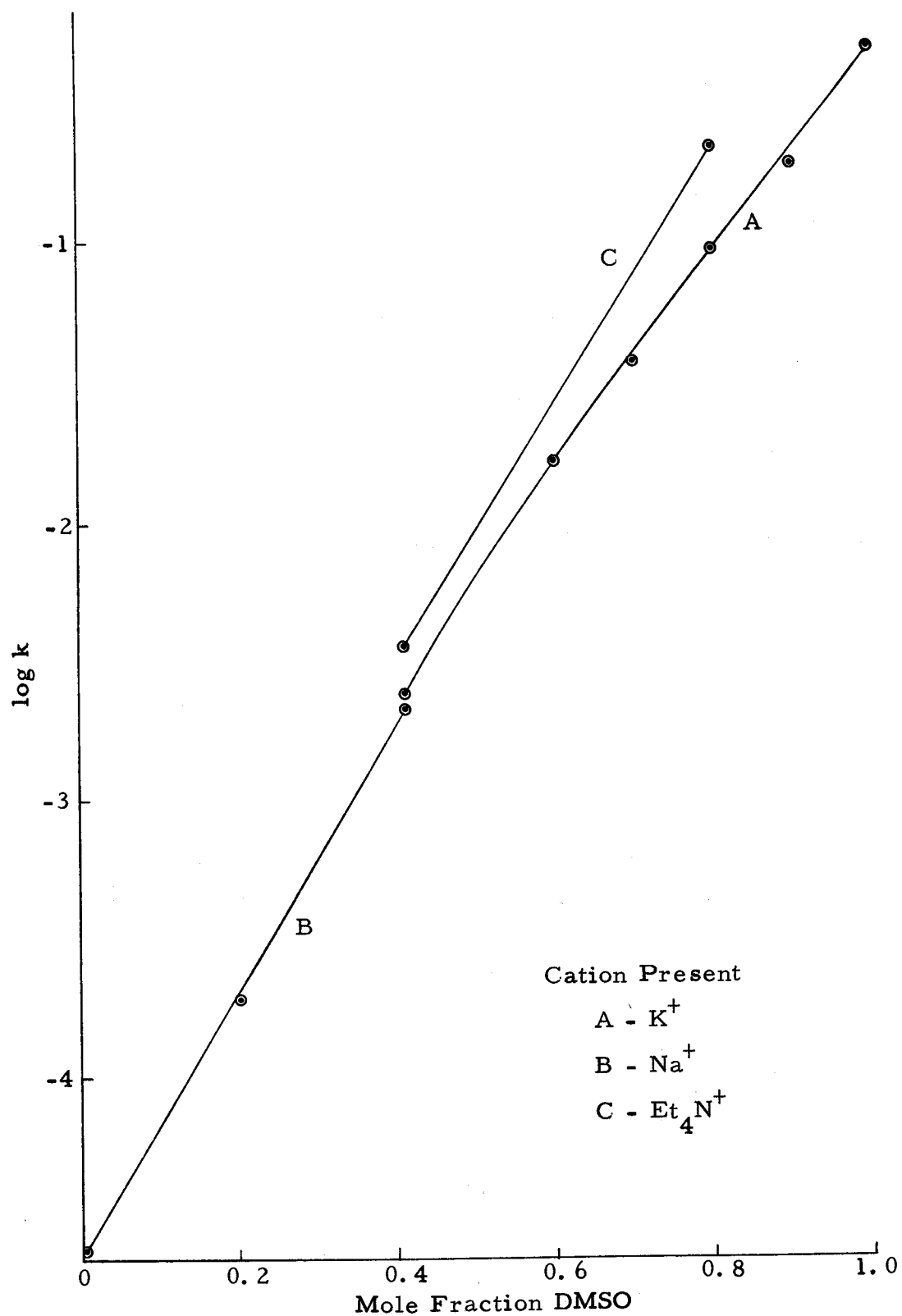


Figure 1. Effect of Solvent on First Order Rate Constant

in a relatively regular manner as one proceeds from pure DMSO to pure water.

The relationship between the rate constant and the dielectric constant of the medium is shown in Figure 2. Here, it is clear that the dielectric constant is not the only factor affecting the rate when the solvent is less than 80% DMSO, since $\log k$ is not a linear function of $1/D$. Above 80% DMSO, however, the points lie on a straight line. The dielectric constants used in this plot were obtained by interpolation of the data published by Wolford (83) in 1964.

In summary, the rate of this reaction increases by a factor of greater than 10^4 as DMSO is substituted for water as the solvent. This effect is not simply an effect of the dielectric constant of the solvent, so it must be due to some extent, at least, to specific solvation effects. These effects will be discussed in more detail later.

Specific Cation Effect

It will be recalled that when the effect of the solvent was studied, it was necessary to use sodium salts below 75% DMSO in order to keep the ionic strength constant at 0.30. It was thought advisable to have both all sodium and all potassium runs in 75% DMSO. These should have given the same result, even if ionic strength was a factor in the rate. They did not, however, yield

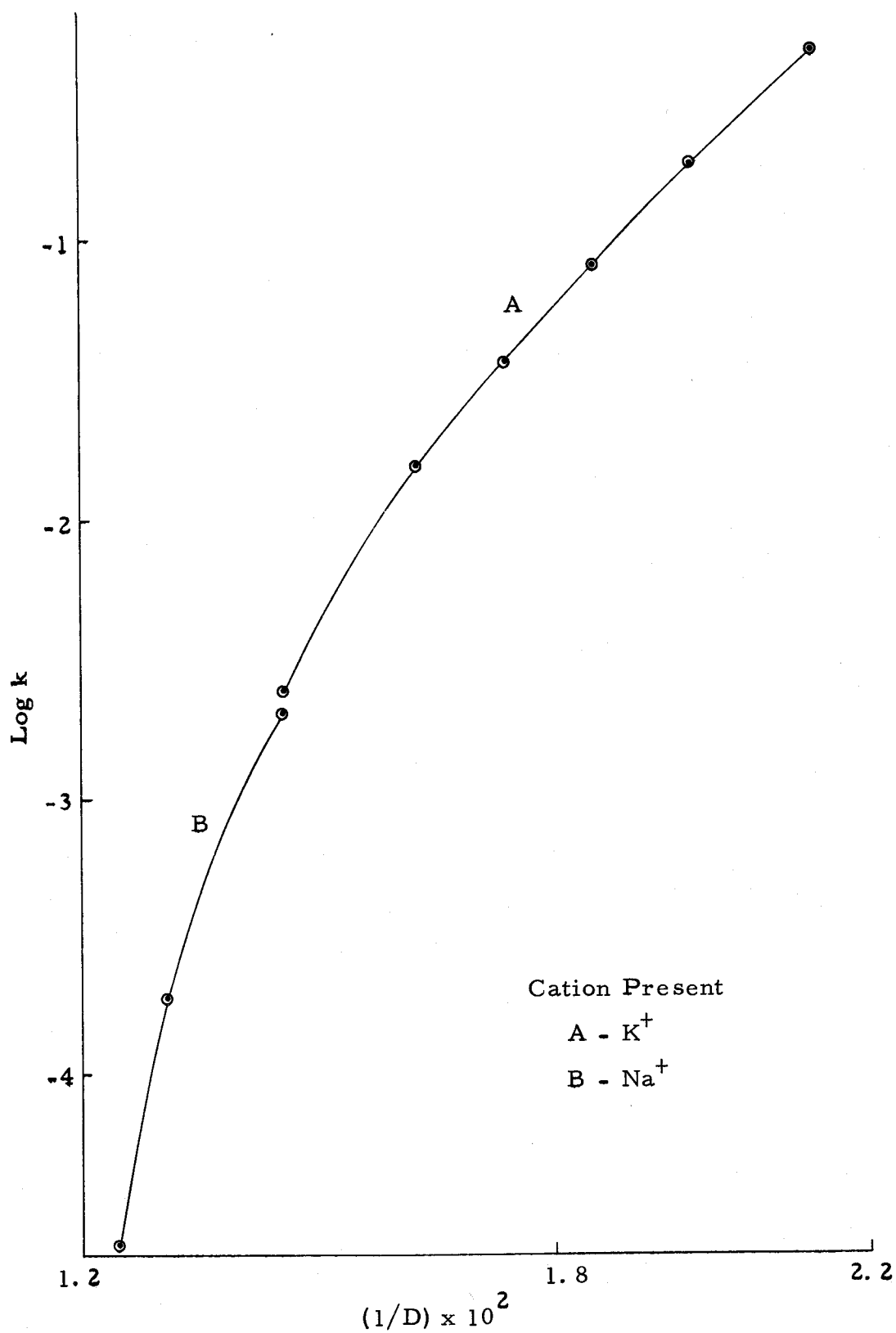


Figure 2. Effect of Dielectric Constant upon the Rate Constant

the same constant. The all sodium salt runs had a somewhat lower rate constant than did the all potassium salt runs in this solvent mixture. See Table 11 and Figure 1. This is an indication of a specific effect due to sodium ions as compared to potassium ions.

An investigation was then undertaken whereby runs were made in which all variables were kept as constant as possible except that other cations were substituted for potassium ions. This was accomplished by progressively substituting other perchlorates for potassium perchlorate in the various samples in a given series of runs. These studies were undertaken both at 75% and 94.55% DMSO. The data is given in Tables 12 through 19. In general the results of this study show that the reaction rates decrease as sodium, lithium and barium ions are substituted for potassium ion, but that rates increase as tetraethylammonium ions were substituted for potassium ions. This is as would be expected, if the effect was due to ion-pair formation between the cation and the formate ion. If one assumes either that the ion pair does not react, or that it reacts slower than does the free formate ion, then the more ion-pairing that occurs the slower is the overall reaction rate. In the ensuing table K_K , K_{Na} , K_{Li} , and K_{Ba} are the dissociation constants for the potassium formate, sodium formate, lithium formate, and barium formate ion-pairs, respectively. The method of calculating the values for these constants will be described later.

Table 12. Kinetic Data for Mixed Tetraethylammonium and Potassium Ion Runs in 75.00% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^2 [\text{HCOO}^-], \text{M}$	$[\text{Et}_4\text{N}^+], \text{M}$	$[\text{K}^+], \text{M}$	$10^3 k, \text{sec}^{-1}$	K_K
2.86	6.01	2.01	.044	0.256	2.47	0.55
2.86	6.01	2.01	.088	0.212	2.71	0.43
2.86	6.01	2.01	.176	0.124	2.92	0.43
2.86	6.01	2.01	.220	0.080	3.25	0.52
3.51	4.86	0.97	.059	0.200	2.59	0.45
3.51	4.86	0.97	.059	0.160	2.73	0.43
3.51	4.86	0.97	.059	0.120	2.90	0.41
3.51	4.86	0.97	.059	0.080	3.06	0.36
3.51	4.86	0.97	.059	0.040	3.31	0.31

Average $K_K = 0.44$

Standard Deviation = 0.07

Table 13. Kinetic Data for Mixed Sodium and Potassium Runs in 75.00% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^2 [\text{HCOO}^-], \text{M}$	$[\text{K}^+], \text{M}$	$[\text{Na}^+], \text{M}$	$10^3 k, \text{sec}^{-1}$	K_{Na}
2.41	5.97	2.20	0.256	0.044	2.22	0.30
2.41	5.97	2.20	0.212	0.088	2.18	0.32
2.41	5.97	2.20	0.169	0.131	2.17	0.35
2.41	5.97	2.20	0.081	0.219	2.03	0.32
2.41	5.97	2.20	0.168	0.132	2.08	0.30
2.41	5.97	2.20	0.124	0.176	1.95	0.26
2.41	5.97	2.20	0.080	0.220	2.01	0.31

Average $K_{\text{Na}} = 0.31$

Standard Deviation = 0.03

Table 14. Kinetic Data for Mixed Potassium and Lithium Ion Runs in 75.00% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^2 [\text{HCOO}^-], \text{M}$	$10^2 [\text{K}^+], \text{M}$	$10^2 [\text{Li}^+], \text{M}$	$10^3 k, \text{sec}^{-1}$	K_{Li}
1.82	6.67	1.99	8.6	21.3	1.89	0.26
1.82	6.67	1.99	13.0	17.0	1.84	0.22
1.82	6.67	1.99	17.2	12.8	2.11	0.31
1.82	6.67	1.99	21.5	8.5	1.95	0.18
1.82	6.67	1.99	25.8	4.25	2.16	0.23
2.78	6.67	1.34	25.6	4.40	2.14	0.21
2.78	6.67	1.34	21.2	8.80	2.05	0.23
2.78	6.67	1.34	16.8	13.2	1.99	0.24
2.78	6.67	1.34	12.4	17.6	2.01	0.29
2.78	6.67	1.34	8.0	22.0	1.98	0.30

Average $K_{\text{Li}} = 0.25$

Standard Deviation = 0.04

Table 15. Kinetic Data for Mixed Potassium and Barium Runs in 75.00% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^2 [\text{HCOO}^-], \text{M}$	$10^2 [\text{K}^+], \text{M}$	$10^2 [\text{Ba}^{2+}], \text{M}$	$10^3 k, \text{sec}^{-1}$	K_{Ba}
3.53	6.67	2.64	9.4	6.96	2.00	0.090
3.53	6.67	2.64	13.5	5.57	2.00	0.082
3.53	6.67	2.64	17.6	4.18	2.08	0.084
3.53	6.67	2.64	21.8	2.78	2.11	0.075
3.53	6.67	2.64	25.9	1.39	2.17	0.064
3.53	6.67	1.43	21.2	2.92	2.07	0.076
3.53	6.67	1.43	16.8	4.39	2.02	0.082
3.53	6.67	1.43	12.5	5.85	2.02	0.093
3.53	6.67	1.43	8.1	7.31	1.91	0.086

Average $K_{\text{Ba}} = 0.081$

Standard Deviation = 0.007

Table 16. Kinetic Data for Mixed Potassium and Tetraethylammonium Runs in 94.55% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^2 [\text{HCOO}^-], \text{M}$	$[\text{Et}_4\text{N}^+], \text{M}$	$[\text{K}^+], \text{M}$	$10^2 k, \text{sec}^{-1}$	K_{K}
3.68	5.99	1.06	---	0.301	8.12	0.19
3.68	5.99	1.06	0.048	0.252	8.95	0.18
3.68	5.99	1.06	0.096	0.204	10.02	0.18
3.68	5.99	1.06	0.143	0.157	12.60	0.23
3.68	5.99	1.06	0.191	0.109	15.05	0.27
3.68	5.99	1.06	0.239	0.061	17.26	0.27
3.53	8.01	1.00	0.218	0.082	15.25	0.21
3.53	8.01	1.00	0.175	0.125	12.80	0.19
3.53	8.01	1.00	0.124	0.176	11.20	0.20
3.53	8.01	1.00	0.087	0.213	9.64	0.18
3.53	8.01	1.00	0.044	0.256	8.55	0.17
3.10	7.35	1.01	---	0.300	7.78	0.17
3.10	7.35	1.01	0.045	0.255	8.55	0.17
3.10	7.35	1.01	0.090	0.210	10.10	0.19
3.10	7.35	1.01	0.135	0.165	11.27	0.19
3.10	7.35	1.01	0.180	0.120	12.93	0.19
3.10	7.35	1.01	0.225	0.075	15.66	0.21

Average $K_{\text{K}} = 0.21$

Standard Deviation = 0.03

Table 17. Kinetic Data for Mixed Sodium and Potassium Runs in 94, 55% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^3 [\text{HCOO}^-], \text{M}$	$[\text{K}^+], \text{M}$	$[\text{Na}^+], \text{M}$	$10^2 k, \text{sec}^{-1}$	K_{Na}
2.20	10.00	1.93	0.261	0.039	7.11	0.058
2.20	10.00	1.93	0.221	0.079	6.57	0.070
2.20	10.00	1.93	0.201	0.098	6.15	0.066
2.20	10.00	1.93	0.181	0.118	5.85	0.069
2.20	10.00	1.93	0.142	0.157	5.45	0.072
2.20	10.00	1.93	0.102	0.197	4.99	0.072
1.72	6.65	2.17	0.253	0.046	7.32	0.073
1.72	6.65	2.17	0.161	0.138	5.97	0.079
1.72	6.65	2.17	0.114	0.185	5.06	0.070
1.72	6.65	2.17	0.069	0.231	4.50	0.068

Average $K_{\text{Na}} = 0.070$

Standard Deviation = 0.05

Table 18. Kinetic Data for Mixed Lithium and Potassium Runs in 94, 55% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^3 [\text{HCOO}^-], \text{M}$	$[\text{K}^+], \text{M}$	$[\text{Li}^+], \text{M}$	$10^2 k, \text{sec}^{-1}$	K_{Li}
1.61	6.69	1.16	0.254	0.047	7.27	0.073
1.61	6.69	1.16	0.208	0.093	5.96	0.062
1.61	6.69	1.16	0.161	0.140	5.32	0.064
1.61	6.69	1.16	0.114	0.187	5.42	0.080
1.61	6.69	1.16	0.068	0.234	4.88	0.078
1.94	6.01	0.90	0.205	0.095	5.64	0.055
1.94	6.01	0.90	0.157	0.143	5.10	0.061
1.94	6.01	0.90	0.061	0.239	4.70	0.075
3.34	5.99	0.99	0.200	0.100	6.00	0.065
3.34	5.99	0.99	0.172	0.128	5.54	0.067
3.34	5.99	0.99	0.144	0.156	5.15	0.065
3.34	5.99	0.99	0.117	0.183	4.79	0.065
3.34	5.99	0.99	0.089	0.211	4.60	0.067
3.34	5.99	0.99	0.061	0.239	4.60	0.073

Average $K_{\text{Li}} = 0.068$

Standard Deviation = 0.007

Table 19. Kinetic Data for Mixed Barium and Potassium Runs in 94.55% DMSO at 20.7°C

$10^5 [I_2], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$[K^+]$	$[Ba^{2+}]$	$10^2 k, sec^{-1}$	K_{Ba}
2.21	6.65	4.12	0.256	0.015	6.87	0.018
2.21	6.65	4.12	0.209	0.031	5.40	0.015
2.21	6.65	4.12	0.163	0.046	4.72	0.016
2.21	6.65	4.12	0.107	0.062	4.29	0.017
2.21	6.65	4.12	0.069	0.077	3.73	0.017
2.53	6.02	0.93	0.062	0.080	3.01	0.014
2.53	6.02	0.93	0.108	0.064	3.51	0.014
2.53	6.02	0.93	0.157	0.048	3.60	0.012
2.53	6.02	0.93	0.205	0.032	3.70	0.009
2.53	6.02	0.93	0.253	0.016	6.47	0.016
3.34	5.99	0.98	0.252	0.016	5.82	0.011
3.34	5.99	0.98	0.204	0.032	4.58	0.012
3.34	5.99	0.98	0.156	0.048	3.51	0.011
3.34	5.99	0.98	0.108	0.064	3.35	0.013
3.34	5.99	0.98	0.060	0.080	3.03	0.014

Average $K_{Ba} = 0.014$

Standard Deviation = 0.003

The question as to whether tetraethylammonium cations also form ion-pairs with the formate ions could, perhaps, be answered by varying the amount of this cation without varying the amount of some other cation. To do this, ionic strength must also be varied at the same time. If the rate of reaction changes with varying the amounts of this cation, it could either be due to ion-pairing or due to an ionic strength effect. If the rate constant is not changed, however, we can conclude that either (1) there is neither a real ionic strength effect nor ion-pairing by tetraethylammonium ion or (2) that these effects cancel each other. The latter case does not seem likely. Thus, runs were set up in which the ionic strength

was varied by means of tetraethylammonium perchlorate at 75% and 94.55% DMSO. The results are listed in Table 20.

Table 20. Results of Varying Ionic Strength by Use of Tetraethylammonium Perchlorate at 20.7°C

Solvent - 75.00% DMSO				
$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^3 [\text{HCOO}^-], \text{M}$	$[\text{Et}_4\text{N}^+], \text{M}$	$10^3 k, \text{sec}^{-1}$
3.29	1.42	2.81	0.000	3.31
3.29	1.42	2.81	0.046	3.36
3.29	1.42	2.81	0.093	3.34
3.29	1.42	2.81	0.185	3.43
3.29	1.42	2.81	0.232	3.47
3.29	1.42	2.81	0.139	3.46
Solvent - 94.55% DMSO				
$10^5 [\text{I}_3^-], \text{M}$	$[\text{I}^-], \text{M}$	$10^3 [\text{HCOO}^-], \text{M}$	$[\text{Et}_4\text{N}^+], \text{M}$	$10^1 k, \text{sec}^{-1}$
3.89	0.100	1.03	0.0000	1.32
3.89	0.100	1.03	0.0484	1.33
3.89	0.100	1.03	0.0969	1.36
3.89	0.100	1.03	0.145	1.34
3.89	0.100	1.03	0.194	1.33
3.89	0.100	1.03	0.242	1.35

Apparently the rate constant remains relatively unchanged as the amount of tetraethylammonium ion is increased. This indicates that there is neither an observable ionic strength effect nor an effect due to ion-pairing of tetraethylammonium ions to formate ions.

Runs were then made at 75.00 and 94.55% DMSO using only tetraethylammonium compounds to obtain a value of the rate constant with no noticeable ion-pairing. The data is listed in Tables 21 and 22.

Table 21. Kinetic Data for All Tetraethylammonium Ion Runs in 75.00% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^2 [HCOO^-], M$	Ionic Strength	$10^3 k, \text{sec}^{-1}$
3.02	8.05	1.95	0.100	3.67
3.02	8.05	1.75	0.098	3.64
3.02	8.05	1.56	0.096	3.69
3.02	8.05	1.36	0.094	3.65
3.02	8.05	1.17	0.092	3.72
3.02	8.05	0.97	0.090	3.72
3.25	15.5	1.95	0.300	3.85
3.25	15.5	2.34	0.300	3.82
3.25	15.6	2.73	0.300	3.85
3.25	15.6	3.11	0.300	3.78
3.25	15.6	3.50	0.300	3.82
3.25	15.6	3.89	0.300	3.84
3.51	4.86	0.97	0.058	3.62
3.51	4.92	0.97	0.059	3.70
3.33	4.67	0.87	0.056	3.58

Average $k = 3.73 \times 10^{-3} \text{ sec}^{-1}$ Standard Deviation = 0.09×10^{-3} or 2.5%

Table 22. Kinetic Data for All Tetraethylammonium Runs in 94.55% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^4 [HCOO^-], M$	Ionic Strength	$10^2 k, \text{sec}^{-1}$
5.05	1.12	3.63	0.250	19.4
5.05	1.12	4.35	0.249	20.2
5.05	1.12	5.07	0.249	20.5
5.05	1.12	5.79	0.249	20.8
5.05	1.12	6.51	0.249	21.3
5.05	1.12	7.23	0.248	21.2
3.37	1.55	4.86	0.305	21.8
3.37	1.54	5.83	0.304	21.8
3.37	1.53	6.80	0.303	21.6
3.37	1.52	7.77	0.301	20.8
3.37	1.51	8.74	0.300	20.9
3.37	1.50	9.71	0.299	20.7
2.97	1.50	9.69	0.151	21.8
3.37	1.52	9.69	0.152	22.2
3.37	1.41	9.65	0.151	22.0

Average $k = 21.1 \times 10^{-2} \text{ sec}^{-1}$ Standard Deviation = 0.7×10^{-2} or 3.4%

If one then assumes that any deviation from this value is due to unreactive ion-pairs, one can then calculate approximate values for the dissociation constant for the various types of ion pairs. This was then done using data from three types of runs and for four different cations, namely, K^+ , Na^+ , Li^+ and Ba^{2+} .

In the first type, (Type 1), all samples contained initially the same concentrations of iodine, tetraethylammonium formate and tetraethylammonium iodide. However, the samples contained varying amounts of the perchlorate of the metal. The ionic strength was not kept constant. The data for these runs is found in Tables 23 through 28. The value for the association constant (K_M) for the metal formate ion-pair was then calculated using the following formula (See Appendix II):

$$(8) \quad K_M = \frac{k}{k_o} Fo_T + \left(\frac{k}{k_o - k} \right) M_T$$

In this formula k is the rate constant for that particular sample, k_o is the rate constant for the sample containing no metal perchlorate, and M_T is the total concentration of the metal perchlorate. Fo_T is the total concentration of formates in the sample.

The second type, (Type 2), consists of runs in which all samples contained the same concentration of iodine, potassium iodide and potassium formate. The various samples, however, had varying

Table 23. Kinetic Data for the Potassium Ion Variation Run in 75.00% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$[K^+]$	$10^3 k, \text{sec}^{-1}$	K_K
3.51	4.86	9.73	0.200	2.59	0.50
3.51	4.86	9.73	0.160	2.73	0.48
3.51	4.86	9.73	0.120	2.90	0.48
3.51	4.86	9.73	0.080	3.06	0.43
3.51	4.86	9.73	0.040	3.31	0.42
3.51	4.86	9.73	0.000	3.62	----

Average $K_K = 0.46$

Standard Deviation = 0.03

Table 24. Kinetic Data for the Lithium Ion Variation Run in 75.00% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$[Li^+]$	$10^3 k, \text{sec}^{-1}$	K_{Li}
3.51	4.92	9.71	0.195	2.21	0.28
3.51	4.92	9.71	0.156	2.39	0.28
3.51	4.92	9.71	0.117	2.62	0.28
3.51	4.92	9.71	0.078	2.90	0.27
3.51	4.92	9.71	0.039	3.27	0.29
3.51	4.92	9.71	0.000	3.70	----

Average $K_{Li} = 0.28$

Standard Deviation = 0.006

Table 25. Kinetic Data for the Barium Ion Variation Run in 75.00% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$[Ba^{2+}], M$	$10^3 k, \text{sec}^{-1}$	K_{Ba}
3.33	4.67	8.73	6.72	2.01	0.081
3.33	4.67	8.73	5.38	2.23	0.083
3.33	4.67	8.73	4.03	2.38	0.074
3.33	4.67	8.73	2.69	2.74	0.081
3.33	4.67	8.73	1.34	3.13	0.086
3.33	4.67	8.73	0.00	3.58	-----

Average $K_{Ba} = 0.081$

Standard Deviation = 0.004

Table 26. Kinetic Data for the Potassium Ion Variation Runs in 94.55% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^1 [\text{I}^-], \text{M}$	$10^4 [\text{HCOO}^-], \text{M}$	$10^1 [\text{K}^+], \text{M}$	$10^2 k, \text{sec}^{-1}$	K_K
3.37	1.27	9.69	2.89	7.67	0.16
3.37	1.31	9.68	2.39	9.01	0.17
3.37	1.36	9.68	1.79	10.79	0.17
3.37	1.41	9.67	1.19	13.19	0.18
3.37	1.45	9.66	0.60	16.61	0.19
3.37	1.50	9.65	0.00	21.95	----

Average $K_K = 0.17$

Standard Deviation = 0.01

Table 27. Kinetic Data for the Lithium Ion Variation Run in 94.55% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^1 [\text{I}^-], \text{M}$	$10^4 [\text{HCOO}^-], \text{M}$	$10^2 [\text{Li}^+], \text{M}$	$10^2 k, \text{sec}^{-1}$	K_{Li}
3.37	1.49	9.69	13.9	7.99	0.078
3.37	1.50	9.69	11.1	9.21	0.078
3.37	1.50	9.69	8.34	10.83	0.079
3.37	1.51	9.69	5.56	13.27	0.082
3.37	1.51	9.69	2.78	16.56	0.082
3.37	1.52	9.69	0.00	22.15	-----

Average $K_{\text{Li}} = 0.080$

Standard Deviation = 0.003

Table 28. Kinetic Data for the Barium Ion Variation Run in 94.55% DMSO at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^1 [\text{I}^-], \text{M}$	$10^4 [\text{HCOO}^-], \text{M}$	$10^2 [\text{Ba}^{2+}], \text{M}$	$10^2 k, \text{sec}^{-1}$	K_{Ba}
2.97	1.51	8.55	4.36	6.13	0.017
2.97	1.50	9.69	3.29	6.91	0.015
2.97	1.50	9.69	2.47	8.06	0.014
2.97	1.50	9.69	1.65	10.32	0.014
2.97	1.50	9.69	0.82	13.72	0.013
2.97	1.50	9.69	0.00	21.75	----

Average $K_{\text{Ba}} = 0.015$

Standard Deviation = 0.001

concentrations of potassium perchlorate. The dissociation constant for the potassium formate ion-pair (K_K) was calculated as described previously. These were runs in which the ionic strength was varied using potassium perchlorate. This kinetic data is listed in Tables 29 and 30. The k_o value used in these calculations was the average value found in the runs containing only tetraethylammonium salts.

The third type of runs, (Type 3), were ones in which all samples contained the same concentrations of iodine, potassium iodide and potassium formate. They differed in that they had varying amounts of the perchlorates of potassium and of the other metal, but they all had an ionic strength of 0.30. The kinetic data for these runs is listed in Tables 12 through 19. In order to calculate the dissociation constant for the other metal formate ion-pair, the value of the dissociation constant, (K_K), for the potassium formate ion-pair is required. The value used was the average of all values calculated from other runs. The formula used in this calculation was: (See Appendix II)

$$(9) \quad K_M = (M_T/a) - (k/k_o)Fo_T$$

where

$$(10) \quad a = (k_o/k) - 1 - K_T / [(k/k_o)Fo_T + K_K]$$

Table 29. Kinetic Data for Ionic Strength Variation Runs in 75, 00% DMSO Using Potassium Salts at 20, 7 °C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^2 [HCOO^-], M$	Ionic Strength	$10^3 k, \text{sec}^{-1}$	K_K
2.95	6.22	4.29	.349	2.02	0.39
2.95	6.22	4.29	.300	2.32	0.47
2.95	6.22	4.29	.251	2.46	0.46
2.95	6.22	4.29	.203	2.53	0.40
2.95	6.22	4.29	.145	2.69	0.35
2.93	6.01	2.21	.315	2.15	0.42
2.93	6.01	2.21	.268	2.39	0.43
2.93	6.01	2.21	.222	2.50	0.44
2.93	6.01	2.21	.082	3.18	0.46
3.09	6.67	1.98	.280	2.46	0.53
3.09	6.67	1.98	.242	2.48	0.47
3.09	6.67	1.98	.203	2.66	0.49
3.09	6.67	1.98	.164	2.72	0.43
3.09	6.67	1.98	.125	2.90	0.42
3.09	6.67	1.98	.086	2.95	0.31
3.20	1.82	.208	.331	2.29	0.53
3.20	1.82	.208	.288	2.48	0.57
3.20	1.82	.208	.245	2.64	0.59
3.20	1.82	.208	.202	2.65	0.50
3.20	1.82	.208	.159	2.70	0.42
3.20	1.82	.208	.116	3.05	0.50

Average value for $K_K = 0.46$

Standard Deviation = 0.07

Table 30. Kinetic Results for Ionic Strength Variation Runs in 94.55% DMSO Using Potassium Salts at 20.7°C

$10^5 [\text{I}_3^-], \text{M}$	$10^2 [\text{I}^-], \text{M}$	$10^3 [\text{HCOO}^-], \text{M}$	Ionic Strength	$10^2 k, \text{sec}^{-1}$	K_K
1.73	10.0	1.95	.373	7.38	0.20
1.73	10.0	1.95	.319	8.59	0.22
1.73	10.0	1.95	.265	9.76	0.23
1.73	10.0	1.95	.238	10.8	0.24
1.73	10.0	1.95	.211	12.1	0.28
1.73	10.0	1.95	.157	13.7	0.27
1.73	10.0	1.95	.103	16.5	0.30
2.17	6.99	1.41	.395	6.03	0.16
2.17	6.99	1.41	.331	7.60	0.19
2.17	6.99	1.41	.266	9.30	0.21
2.17	6.99	1.41	.201	10.5	0.20
2.17	6.99	1.41	.136	12.8	0.21
2.17	6.99	1.41	.071	17.1	0.30
3.66	10.3	0.996	.344	7.08	0.17
3.66	10.3	0.996	.296	7.99	0.18
3.66	10.3	0.996	.248	9.06	0.19
3.66	10.3	0.996	.200	10.01	0.18
3.66	10.3	0.996	.152	11.37	0.18
3.66	10.3	0.996	.104	13.14	0.17

Average $K_K = 0.21$

Standard Deviation = 0.04

In this formula K_M is the dissociation constant for the metal formate ion-pair. In the individual cases, it would be K_K , K_{Na} , K_{Li} , or K_{Ba} . M_T is the total concentration of the metal ion other than potassium. K_T is the total potassium ion concentration. Type 3 runs in which the dissociation constant for the potassium formate ion-pair was calculated were ones in which potassium and tetraethylammonium perchlorates were interchanged to maintain constant ionic strength. K_K was calculated from these by means of Equation 8.

A summary of the values obtained for the various metal formate ion-pairs is found in Table 31. There is fair agreement between values for the same dissociation constant obtained by the various methods. The values obtained are all smaller in 94.55% DMSO than those in 75.00% DMSO. The dissociation constant also decreases as the cation gets smaller and increases in charge. It should be pointed out that these values for the dissociation constant for the various types of ion-pairs are calculated on the assumption that the ion-pairs are unreactive.

Temperature Effect

The effect of variation in temperature on the rate of this reaction was measured at 75.00 and 94.55% DMSO as a means of obtaining the value of the enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of

Table 31. Summary of Calculated Dissociation Constants for the Metal Formate Ion-Pairs

% DMSO	Cation	Type of Run ^a	Average K_M
75.00	K^+	1	0.46
75.00	K^+	2	0.46
75.00	K^+	3	0.44
75.00	K^+	all	0.45
75.00	Na^+	3	0.31
75.00	Li^+	1	0.28
75.00	Li^+	3	0.25
75.00	Li^+	all	0.27
75.00	Ba^{2+}	1	0.081
75.00	Ba^{2+}	3	0.081
75.00	Ba^{2+}	all	0.081
94.55	K^+	1	0.17
94.55	K^+	2	0.21
94.55	K^+	3	0.21
94.55	K^+	all	0.20
94.55	Na^+	3	0.070
94.55	Li^+	1	0.080
94.55	Li^+	3	0.068
94.55	Li^+	all	0.071
94.55	Ba^{2+}	1	0.015
94.55	Ba^{2+}	3	0.014
94.55	Ba^{2+}	all	0.014

^aTypes 1, 2, and 3 are as described in the text.

activation. According to Transition State Theory (27, p. 77-101),

$$(11) \quad \ln k_r = \ln(kT/h) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT$$

where k_r is the rate constant, k is the Boltzmann constant, h is Planck's constant, and R is the gas law constant. The plot of the logarithm of the rate constant versus the reciprocal of the absolute temperature should yield an approximate straight line, whose slope is $\frac{E_a}{2.303R}$, where E_a is the activation energy for the reaction. The enthalpy of activation can be calculated using

$$(12) \quad \Delta H^\ddagger = E_a - RT.$$

One can then calculate the value for entropy of activation ($\Delta S^\ddagger$) by substitution into Equation 11.

The effect of temperature on the reaction rate was measured by making some runs at different temperatures in 75.00 and 94.55% DMSO. Some samples containing potassium ion as the only cation were run. In other cases, the only cation was tetraethylammonium ion. The data for these runs is listed in Tables 32 through 43.

These data are summarized in Table 44. Figures 3 and 4 show the relationship between the logarithm of the rate constant and the reciprocal of the absolute temperature.

Table 32. Kinetic Data for All Potassium Ion Runs in 75.00% DMSO at 14.1°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^2 [HCOO^-], M$	$10^4 k, \text{sec}^{-1}$
4.45	10.01	10.05	10.3
4.45	10.01	9.05	10.1
4.45	10.01	8.05	10.0
4.45	10.01	7.05	9.9
4.45	10.01	6.04	9.7
4.45	10.01	5.04	9.6
3.62	10.00	5.00	10.5
3.62	9.00	5.00	10.4
3.62	8.01	5.00	10.3
3.62	7.01	5.00	10.7
3.62	6.01	5.00	10.8
3.62	5.02	5.00	10.0

Ionic Strength = 0.300 ± 0.005 Average $k = 10.2 \times 10^{-4} \text{sec}^{-1}$ Standard Deviation = 0.4×10^{-4}

Table 33. Kinetic Data for All Potassium Ion Runs in 75.00% DMSO at 13.3°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^2 [HCOO^-], M$	$10^4 k, \text{sec}^{-1}$
3.45	3.66	3.31	9.85
3.45	3.66	2.98	8.82
3.45	3.66	2.64	8.73
3.45	3.66	2.31	8.86
3.45	3.66	1.98	8.94
3.45	3.66	1.64	9.19

Ionic Strength = 0.300 ± 0.005 Average $k = 8.91 \times 10^{-4}$ Standard Deviation = 0.16×10^{-4}

Table 34. Kinetic Data for All Potassium Ion Runs in 75.00% DMSO at 25.4°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$10^3 k, \text{sec}^{-1}$
3.87	1.61	1.97	4.00
3.87	1.61	2.36	3.99
3.87	1.61	2.75	3.97
3.87	1.61	3.15	4.00
3.87	1.61	3.54	3.98
3.87	1.61	3.93	4.00

Ionic Strength = 0.300 ± 0.005 Average $k = 3.99 \times 10^{-3} \text{sec}^{-1}$ Standard Deviation = 0.02×10^{-3}

Table 35. Kinetic Data for All Potassium Ion Runs in 75.00% DMSO at 30.5°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^3 [HCOO^-], M$	$10^3 k, \text{sec}^{-1}$
3.54	0.200	6.61	7.58
3.54	0.180	6.61	7.39
3.54	0.160	6.61	7.50
3.54	0.140	6.61	7.16
3.54	0.120	6.61	6.92
3.54	0.100	6.61	6.70
3.08	0.100	6.66	6.92
3.08	0.100	9.32	6.92
3.08	0.100	12.00	7.12
3.08	0.100	14.6	7.07
3.08	0.100	17.3	6.92
3.08	0.100	19.9	7.23
3.57	0.100	11.5	7.34
3.57	0.100	8.96	7.27
3.57	0.100	6.40	7.31
3.47	0.100	10.2	7.44
3.47	0.120	10.2	7.50
3.47	0.140	10.2	7.55
3.47	0.160	10.2	7.28
3.47	0.180	10.2	7.35
3.47	0.200	10.2	7.58

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.25×10^{-3}

Average $k = 7.24 \times 10^{-3} \text{sec}^{-1}$

Table 36. Kinetic Data for All Potassium Ion Run in 94.55% DMSO at 14.0°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$10^2 k, \text{sec}^{-1}$
4.20	10.01	0.89	4.14
4.20	10.01	1.06	3.96
4.20	10.01	1.24	3.96
4.20	10.01	1.42	4.20
4.20	10.01	1.59	4.20
4.20	10.01	1.76	4.26

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.13×10^{-2}

Average $k = 4.12 \times 10^{-2} \text{sec}^{-1}$

Table 37. Kinetic Data for All Potassium Ion Run in 94.55% DMSO at 13.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$10^2 k, \text{sec}^{-1}$
4.81	20.0	1.99	4.03
4.81	18.0	1.99	3.96
4.81	16.0	1.99	4.08
4.81	14.0	1.99	4.00
4.81	12.0	1.99	3.99
4.81	10.0	1.99	4.04

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.04×10^{-2}

Average $k = 4.02 \times 10^{-2} \text{sec}^{-1}$

Table 38. Kinetic Data for All Potassium Ion Run in 94.55% DMSO at 13.4°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [HCOO^-], M$	$10^2 k, \text{sec}^{-1}$
3.60	10.0	0.91	3.66
3.60	10.0	1.27	3.74
3.60	10.0	1.63	3.74
3.60	10.0	2.00	3.86
3.60	10.0	2.36	3.77
3.60	10.0	2.72	3.79

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.07×10^{-2}

Average $k = 3.76 \times 10^{-2} \text{sec}^{-1}$

Table 39. Kinetic Data for All Potassium Ion Run in 94.55% DMSO at 25.3°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^3 [HCOO^-], M$	$10^1 k, \text{sec}^{-1}$
3.75	2.99	1.19	1.298
3.75	2.99	1.43	1.302
3.75	2.98	1.67	1.300
3.75	2.98	1.91	1.309
3.75	2.98	2.15	1.309
3.75	2.97	2.38	1.307

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.005×10^{-1}

Average $k = 1.304 \times 10^{-1} \text{sec}^{-1}$

Table 40. Kinetic Data for All Potassium Ion Runs in 94.55% DMSO at 30.5°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^4 [HCOO^-], M$	$10^1 k, \text{sec}^{-1}$
3.80	3.00	29.1	2.09
3.80	2.99	25.3	1.98
3.80	2.99	21.4	2.07
3.80	2.98	17.5	2.00
3.80	2.98	13.6	2.08
3.80	2.97	9.72	2.01
2.81	2.99	4.87	1.80
2.81	2.73	4.87	1.86
2.81	2.46	4.87	1.77
2.81	2.20	4.87	1.78
2.81	1.93	4.87	1.75
2.81	1.66	4.87	1.76
3.40	1.66	7.43	1.92
3.40	1.93	7.43	1.92
3.40	2.20	7.43	1.96
3.40	2.46	7.43	1.85
3.40	2.73	7.43	1.87
3.40	2.99	7.43	1.82
4.00	2.98	21.1	2.02
4.00	2.99	18.3	2.03
4.00	2.99	15.5	2.03
4.00	2.99	9.85	2.00
4.00	2.99	7.04	1.97

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.11×10^{-1}

Average $k = 1.93 \times 10^{-1} \text{sec}^{-1}$

Table 41. Kinetic Data for All Tetraethylammonium Runs in 75.00% DMSO at 29.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^2 [HCOO^-], M$	$10^2 k, \text{sec}^{-1}$
3.38	20.1	0.97	1.28
3.38	20.1	1.17	1.23
3.38	20.1	1.36	1.20
3.38	20.1	1.56	1.16
3.38	20.1	1.75	1.16
3.38	20.1	1.95	1.17

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.05×10^{-2}

Average $k = 1.20 \times 10^{-2} \text{sec}^{-1}$

Table 42. Kinetic Data for All Tetraethylammonium Runs in 94.55% DMSO at 14.8°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^3 [HCOO^-], M$	$10^1 k, \text{sec}^{-1}$
3.37	1.51	1.94	1.20
3.37	1.51	1.74	1.20
3.37	1.50	1.55	1.19
3.37	1.50	1.36	1.18
3.37	1.50	1.12	1.15
3.37	1.50	0.97	1.19

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.03×10^{-1}

Average $k = 1.19 \times 10^{-1} \text{sec}^{-1}$

Table 43. Kinetic Data for All Tetraethylammonium Runs in 94.55% DMSO at 30.1°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^3 [HCOO^-], M$	$10^1 k, \text{sec}^{-1}$
3.37	2.21	4.85	5.53
3.37	2.21	5.83	5.70
3.37	2.21	6.80	5.57
3.37	2.21	7.77	5.66
3.37	2.21	8.75	5.78
3.37	2.21	9.72	5.80

Ionic Strength = 0.300 ± 0.005
 Standard Deviation = 0.11×10^{-1}

Average $k = 5.67 \times 10^{-1} \text{sec}^{-1}$

Table 44. Summary of Kinetic Data at Various Temperatures

% DMSO	Cation Present	Temperature	Average k
75.00	K ⁺	14.1°C	1.02×10^{-3}
75.00	K ⁺	13.3°C	0.89×10^{-3}
75.00	K ⁺	20.7°C	2.48×10^{-3}
75.00	K ⁺	25.4°C	3.99×10^{-3}
75.00	K ⁺	30.5°C	7.24×10^{-3}
75.00	Et ₄ N ⁺	20.7°C	3.73×10^{-3}
75.00	Et ₄ N ⁺	29.7°C	1.20×10^{-2}
94.55	K ⁺	14.0°C	4.12×10^{-2}
94.55	K ⁺	13.7°C	4.02×10^{-2}
94.55	K ⁺	13.4°C	3.76×10^{-2}
94.55	K ⁺	20.7°C	8.12×10^{-2}
94.55	K ⁺	25.3°C	13.04×10^{-2}
94.55	K ⁺	30.5°C	1.93×10^{-1}
94.55	Et ₄ N ⁺	14.8°C	1.19×10^{-1}
94.55	Et ₄ N ⁺	20.7°C	2.11×10^{-1}
94.55	Et ₄ N ⁺	30.1°C	5.67×10^{-1}

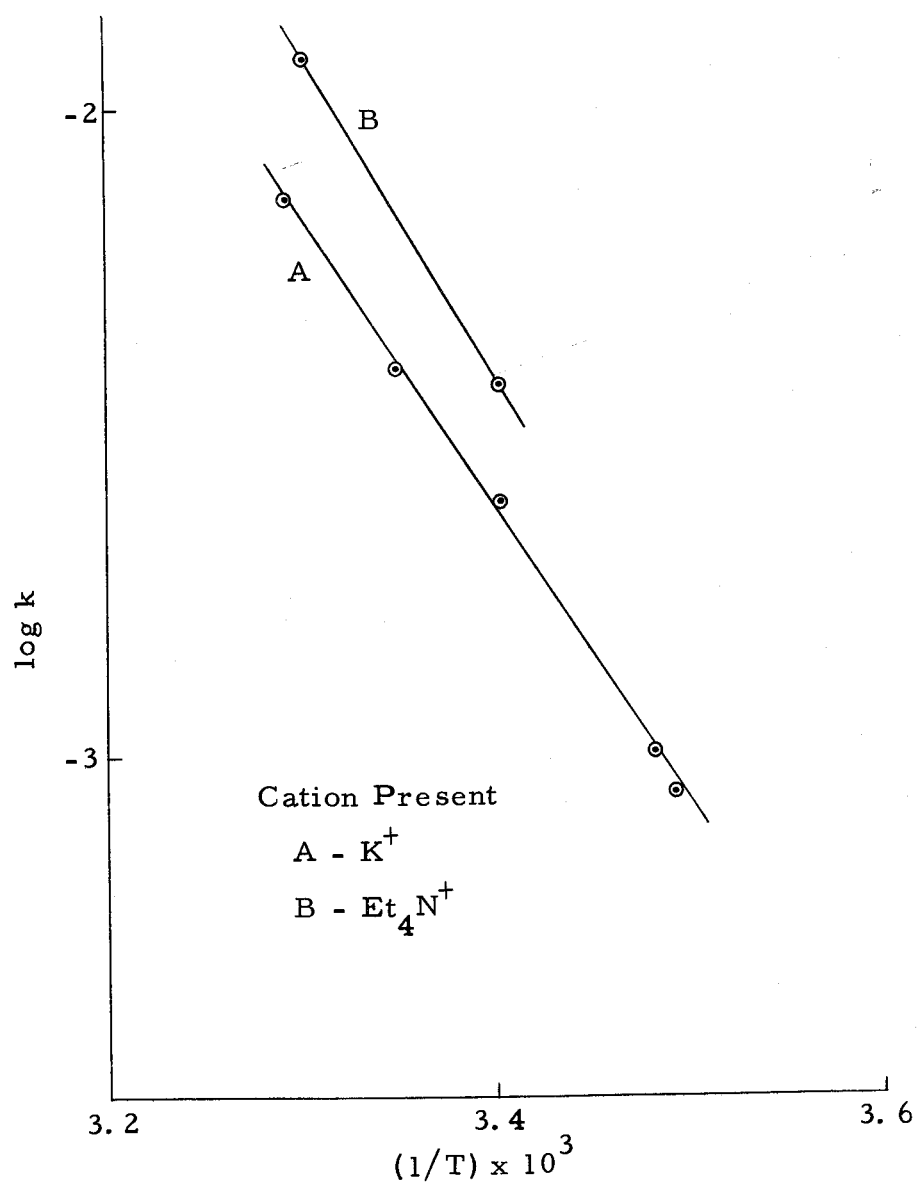


Figure 3. Temperature Dependence of Rate Constant in 75.00% DMSO

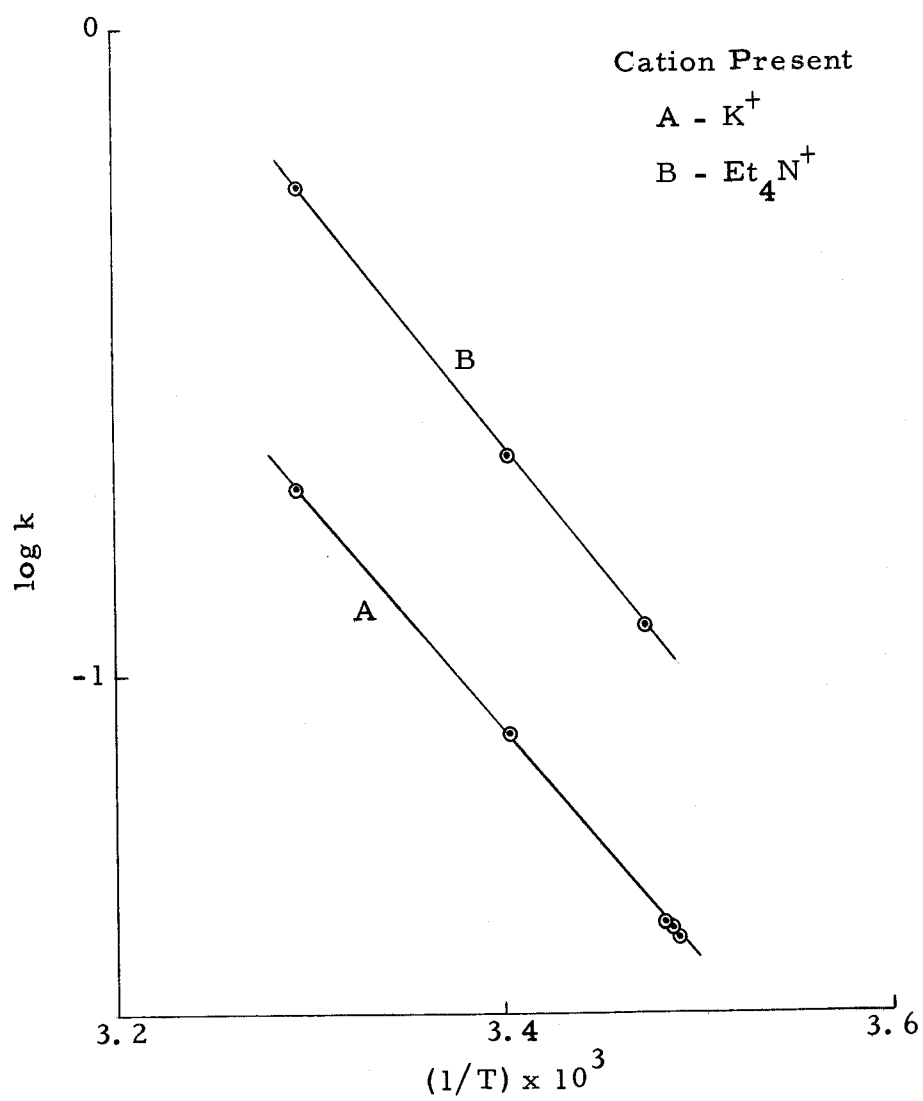


Figure 4. Temperature Dependence of Rate Constant in 94.55% DMSO

The enthalpy and entropy of activation have been determined for these data. The results of these calculations are listed in Table 45. These values were calculated making use of the method of least squares.

Table 45. Calculated Entropies and Enthalpies of Activation for the Iodine-Formate Reaction

% DMSO	Cation	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$, E. U.
75.00	K ⁺	19.6	- 2.8
75.00	Et ₄ N ⁺	22.3	6.4
94.55	K ⁺	15.7	-10.0
94.55	Et ₄ N ⁺	17.3	- 2.8

Briefly, as the solvent changes from 75.00% DMSO to 94.55%, there is a decrease in the enthalpy of activation of 4-5 kcal/mole and a decrease in entropy of activation of about eight entropy units. Changing from potassium to tetraethylammonium ions results in an increase in enthalpy of activation of about 2 kcal/mole and an increase in entropy of activation of about eight entropy units.

Isotope Effect

One of the more important tools which can aid in the elucidation of a reaction mechanism is the kinetic isotope effect. Consequently, a study relating the rate of reaction of iodine

with deuterated sodium formate to that with ordinary sodium formate was undertaken. The comparative rates should yield some information about the importance of the breaking of the carbon-hydrogen bond in the rate determining step. Since carbon to deuterium bonds are stronger than carbon to protium bonds, a step involving the breaking of a carbon to hydrogen bond should be slower if the heavier isotope is used.

Several measurements of the effect of substituting deuterioformate for regular formate in the iodine-formate reaction for several different solvent compositions have been conducted. The kinetic results are listed in Tables 46 through 50 and the average k_H/k_D values are listed in Table 51.

These values are considerably smaller than 6.9 for complete bond breaking for a carbon to hydrogen bond (78). One can conclude that the carbon-hydrogen bond is not completely broken in the activated complex, but has been weakened. Furthermore, this study shows a reduction of the k_H/k_D ratio as the water content of the solvent decreases.

Triiodide Association Constant

Since this reaction involves iodine in the presence of iodide ions, and since one of the important equilibria taking place in such a system is that involving the formation of triiodide ion from iodine

Table 46. Kinetic Results for Formate-Deuteroformate Run in Water at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^1 [HCOO^-], M$	$10^1 [DCOO^-], M$	$10^6 k, \text{sec}^{-1}$
3.81	1.02	----	2.90	5.64
3.81	1.02	----	2.90	5.53
3.81	1.02	2.90	----	21.1
3.81	1.02	2.90	----	21.2
3.81	1.02	2.90	----	21.3
Average $k_D = 5.58 \times 10^{-6} \text{sec}^{-1}$		Average $k_H = 2.12 \times 10^{-5} \text{sec}^{-1}$		
$k_H/k_D = 3.8 \pm 0.3$				

Table 47. Kinetic Results for Deuteroformate Runs in 75.00% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^2 [DCOO^-], M$	$10^4 k, \text{sec}^{-1}$
3.52	5.00	9.96	7.92
3.52	5.00	8.51	7.60
3.52	5.00	7.06	7.83
3.52	5.00	5.61	7.73
3.52	5.00	4.15	7.67
3.52	5.00	2.70	7.70
3.35	2.60	2.09	8.17
3.35	2.33	2.09	8.08
3.35	2.06	2.09	7.93
3.35	1.80	2.09	8.13
3.35	1.53	2.09	8.06
3.35	1.27	2.09	8.14
Average $k_D = 7.91 \times 10^{-4} \text{sec}^{-1}$		Standard Deviation = 0.20×10^{-4}	
$k_H/k_D = 2.9 \pm 0.2$			

Table 48. Kinetic Results for Deuteroformate Runs in 94.55% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^2 [I^-], M$	$10^3 [DCOO^-], M$	$10^2 k, \text{sec}^{-1}$
3.66	10.0	1.62	3.09
3.66	10.0	2.25	3.14
3.66	10.0	2.87	3.13
3.66	10.0	3.50	3.24
3.66	10.0	4.12	3.20
3.66	10.0	4.75	3.27
3.84	20.0	0.81	3.23
3.84	18.0	0.81	3.12
3.84	16.0	0.81	3.08
3.84	14.0	0.81	3.21
.84	12.0	0.81	3.20
3.84	10.0	0.81	3.17
Average $k_D = 3.17 \times 10^{-2} \text{sec}^{-1}$		Standard Deviation = 0.06×10^{-2}	
$k_H/k_D = 2.5 \pm 0.2$			

Table 49. Kinetic Results for Formate-Deuteroformate Comparison Runs in 97.50% DMSO at 20.7°C

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^3 [HCOO^-], M$	$10^3 [DCOO^-], M$	$10^2 k, \text{sec}^{-1}$	k_H/k_D
3.66	2.98	1.80	----	19.0	2.41
3.66	2.98	----	1.79	7.86	
3.66	2.98	1.80	----	18.7	2.40
3.66	2.98	----	1.79	7.78	
3.66	2.98	1.80	----	18.2	2.34
3.66	2.98	----	1.79	7.78	
3.66	2.98	1.80	----	18.8	2.41
3.66	2.98	----	1.79	7.81	

Average $k_H/k_D = 2.4 \pm 0.1$

Table 50. Kinetic Results for Formate-Deuteroformate Comparison Run in 100% DMSO

$10^5 [I_3^-], M$	$10^1 [I^-], M$	$10^3 [HCOO^-], M$	$10^4 [DCOO^-], M$	$10^1 k, \text{sec}^{-1}$	k_H/k_D
3.70	2.99	6.00	----	4.64	2.17
3.70	3.00	----	6.03	2.14	
3.70	3.00	----	6.03	2.16	2.15
3.70	2.99	6.00	----	4.64	
3.70	2.99	6.00	----	4.65	2.18
3.70	3.00	----	6.03	2.13	
3.70	3.00	----	6.03	2.13	2.13
3.70	2.99	6.00	----	4.54	

Average $k_H/k_D = 2.16 \pm 0.1$ Table 51. k_H/k_D for Various Solvent Compositions in the Iodine-Formate Reactions at 20.7°C

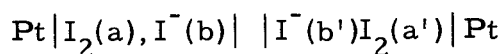
% DMSO	k_H/k_D
0.00	3.8
75.00	2.9
94.55	2.5
97.50	2.4
100.00	2.2

molecules and iodide ions,



it is useful to know something about the effect of the change in solvent upon this equilibrium. The association constant for triiodide ion has been determined in aqueous solution by numerous investigators (2, 13, 62).

Measurements of this association constant were made in four different solvent mixtures. A method similar to one used by Parker in dimethylformamide (DMF) and in methanol (58) was employed. This method consists of measuring the potential of a cell, consisting of platinum electrodes and both electrolytes containing a mixture of iodine and potassium iodide. In one half cell the concentration of iodine is greater than that of potassium iodide and in the other, less. The standard way of expressing this cell is



where $a > b$ and $b' > a'$.

The association constant for triiodide ion can be calculated from this cell provided that one assumes that the activity coefficients of iodide and triiodide ions are the same. The data from these experiments are listed in Tables 52 through 59 and summarized in Table 60. A literature value (13) for this constant in water is included for comparison purposes.

Table 52. Results of Triiodide Association Constant Determinations in 52.02% DMSO at 23°C

Cell 1		Cell 2			
a	b	a'	b'	E(mV)	$10^{-3} K_a$
0.07553	0.05911	0.01524	0.09730	207	6.0
0.07553	0.05911	0.05359	0.18210	251	6.1
0.07553	0.05911	0.02085	0.07725	191	6.2
0.07271	0.06874	0.00723	0.16430	193	5.1
0.05402	0.05530	0.00504	0.22611	172	4.7

Average $K_a = 5.5 \times 10^3$

Standard Deviation = 0.7×10^3

Table 53. Results of Triiodide Association Constant Determinations in 75.00% DMSO at 22°C
Using No Salt Bridge

Cell 1		Cell 2			
a	b	a'	b'	E(m)	$10^{-5} K_a$
0.10634	0.01931	0.00950	0.10072	416	0.82
0.10638	0.01868	0.00340	0.10532	435	0.97
0.14066	0.00737	0.00846	0.11622	464	0.96
0.09979	0.04881	0.04395	0.10593	342	1.23
0.10703	0.01580	0.02541	0.09211	407	1.37
0.05199	0.00770	0.00356	0.26354	469	1.10

Average $K_a = 1.04 \times 10^5$

Standard Deviation = 0.15×10^5

Table 54. Results of Triiodide Association Constant Determinations in 75.00% DMSO at 22°C
Using 0.1M Et₄NCIO₄ Solution as a Salt Bridge

Cell 1		Cell 2			
a	b	a'	b'	E(mV)	10 ⁻⁵ K _a
0.13343	0.00904	0.01193	0.10454	437	0.82
0.05976	0.01676	0.01738	0.08339	363	0.82
0.19500	0.00705	0.00433	0.24112	508	0.83
0.13343	0.00904	0.00433	0.24112	497	1.11
0.05976	0.01676	0.01193	0.10454	388	0.99
0.19500	0.00705	0.01738	0.08339	452	1.09
0.09690	0.00868	0.01034	0.10074	440	1.15
0.09690	0.00484	0.01034	0.10074	452	1.01
0.09690	0.03036	0.01034	0.10074	393	1.02
0.09690	0.00304	0.01034	0.10074	464	1.00
0.09690	0.01990	0.01034	0.10074	409	1.10
0.09690	0.00745	0.01034	0.10074	442	1.07
0.09690	0.00868	0.01034	0.10074	437	1.05

Average K_a = 1.00 x 10⁵

Standard Deviation = 0.11 x 10⁵

Table 55. Results of Triiodide Association Constant Determinations in 75.00% DMSO at 30°C
Using 0.1M Et₄NCIO₄ as a Salt Bridge

Cell 1		Cell 2			
a	b	a'	b'	E(mV)	10 ⁻⁴ K _a
0.11720	0.00783	0.01774	0.10680	446	8.3
0.07432	0.02722	0.01774	0.10680	376	7.4
0.07432	0.02722	0.02943	0.04712	342	8.4
0.18400	0.03940	0.02943	0.04712	441	6.8
0.18400	0.03940	0.00298	0.24420	530	6.3
0.11720	0.00783	0.00298	0.24420	499	7.4

Average K_a = 7.4 x 10⁴

Standard Deviation = 0.8 x 10⁴

Table 56. Results of Triiodide Association Constant Determinations in 94, 55% DMSO at 22°C
Using No Salt Bridge

Cell 1		Cell 2			
a	b	a'	b'	E(mV)	$10^{-5}K_a$
0.07412	0.02025	0.02693	0.05154	375	3.1
0.12136	0.00990	0.01038	0.10530	476	2.5
0.29640	0.00426	0.00747	0.20930	556	1.9
0.12136	0.00990	0.00747	0.20930	504	2.2
0.29640	0.00426	0.01038	0.10530	528	2.2
0.07412	0.02025	0.00747	0.20930	458	2.2
0.09006	0.04228	0.03346	0.11254	391	3.0
0.10813	0.01342	0.01589	0.10538	457	2.6
0.15098	0.00864	0.00483	0.11888	504	2.4

Average $K_a = 2.4 \times 10^5$

Standard Deviation = 0.4×10^5

Table 57. Results of Triiodide Association Constant Determinations in 94, 55% DMSO at 30°C
Using 0.1M Et₄NC10₄ as a Salt Bridge

Cell 1		Cell 2			
a	b	a'	b'	E(mV)	$10^{-5}K_a$
0.12272	0.01182	0.00915	0.09805	473	2.0
0.05978	0.02202	0.00915	0.09805	417	2.1
0.05978	0.02202	0.02224	0.07858	390	2.2
0.18159	0.00480	0.02224	0.07858	482	1.8
0.18159	0.00480	0.00476	0.22929	548	1.4
0.12272	0.01182	0.00476	0.22929	514	1.7

Average $K_a = 1.9 \times 10^5$

Standard Deviation = 0.3×10^5

Table 58. Results of Triiodide Association Constant Determinations in 100% DMSO at 22°C
Using No Salt Bridge

Cell 1		Cell 2			
a	b	a'	b'	E(mV)	$10^{-5} K_a$
0.08537	0.00943	0.00847	0.09772	443	1.3
0.24858	0.00478	0.00500	0.23285	547	1.3
0.00849	0.02083	0.02426	0.07966	441	1.2
0.24858	0.00478	0.00235	0.06205	533	2.5
0.08537	0.00943	0.00235	0.06205	470	2.7
0.08849	0.02083	0.00500	0.23285	486	2.6

Average $K_a = 1.9 \times 10^5$

Standard Deviation = 0.7×10^5

Table 59. Results of Triiodide Association Constant Determinations in 100% DMSO at 22°C
Using 0.1M Et₄NC₁₀ as a Salt Bridge

Cell 1		Cell 2			
a	b	a'	b'	E(mV)	$10^{-5} K_a$
0.10740	0.00972	0.01137	0.10120	466	2.4
0.10790	0.00972	0.00502	0.20670	501	2.0
0.23890	0.00451	0.00502	0.20670	549	1.8
0.23890	0.00451	0.02819	0.06413	462	2.4
0.01051	0.00528	0.01137	0.10120	359	1.8
0.01051	0.00528	0.00502	0.20670	394	1.4
0.01051	0.00528	0.02819	0.06413	303	1.4

Average $K_a = 1.9 \times 10^5$

Standard Deviation = 0.4×10^5

The standard deviation in a given set of results is around 15%. This is comparable to Parker's results in DMF (58). Sometimes a drift was observed in the voltage reading during the period immediately after the electrodes were first inserted into the half cells. Normally, however, this drift ceased after a minute or two. This drift, however, probably contributed to variation in readings. In general there was little difference in the results if a salt bridge was used as compared to simply a sintered glass partition (no salt bridge).

In general, the dissociation constant of I_3^- in DMSO-water mixtures is much smaller than it is in water. There is a relatively large increase in stability of triiodide ion until 75% DMSO (40 mole percent DMSO) is reached. After that the increase in stability is small.

Table 60. Triiodide Association and Dissociation Constants in Dimethylsulfoxide-Water Mixture

% DMSO	Temperature	Association Constant	Dissociation Constant (K_d)
00.00	20°C	8.24×10^2	1.2×10^{-3}
52.02	23°C	5.5×10^3	1.8×10^{-4}
75.00	22°C	1.02×10^5	9.8×10^{-6}
75.00	30°C	7.4×10^4	1.3×10^{-5}
94.55	22°C	2.4×10^5	4.2×10^{-6}
94.55	30°C	1.9×10^5	5.3×10^{-6}
100.00	22°C	1.9×10^5	5.3×10^{-6}

An estimation of the values for enthalpy and entropy of this reaction was made from the temperature variation data. The results are listed in Table 61.

Table 61. Enthalpy and Entropy Changes for the Triiodide Association in DMSO-Water Mixtures

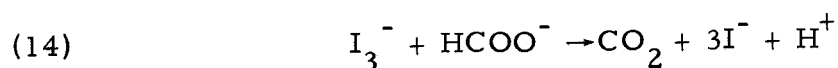
% DMSO	$\Delta H(\text{kcal/mole})$	$\Delta S(\text{E. U.})$
0	-4.8	-2.9
75.00	-7.1	-1.4
94.55	-5.7	6.1

The values for 0% were from Ramette and Sanford's (62) data for comparison purposes.

DISCUSSION

Mechanism

Our results have shown that in DMSO-water mixtures the iodine-formate reaction has the same stoichiometry (Equation 14) as it does in water, namely,



Also, the same rate law observed in DMSO-water mixtures is the same as that observed in water. Namely, that if the concentrations of both the formate and iodide ions are large compared to the concentration of free iodine, the rate law (9, 33) is

$$(15) \quad \frac{-d[\Sigma \text{I}_2]}{dt} = \frac{k_1[\Sigma \text{I}_2][\text{HCOO}^-]}{1 + [\text{I}^-]/K_d},$$

where K_d is the dissociation constant for the triiodide ion. If $[\text{I}^-]$ is also much greater than K_d , this rate law becomes

$$(16) \quad \frac{-d[\Sigma \text{I}_2]}{dt} = \frac{k[\Sigma \text{I}_2][\text{HCOO}^-]}{[\text{I}^-]},$$

where $k = k_1 K_d$.

The latter rate law is the one observed during most of this

study. In all solvent mixtures except in water $[I^-]$ was much greater than K_d . In water, however, the $[I^-]/K_d$ ratio is smaller than it is in other solvent mixtures. This ratio becomes less in water because (1) K_d is larger (Table 60) and (2) because a smaller $[I^-]$ is required to produce a convenient reaction rate.

All of the rate constants listed in the kinetic data are the values of k from Equation 15. These are, therefore, in reality the product, $k_1 K_d$. Thus, any changes in k may be either due to shifting of the triiodide equilibrium or changes in rate of the rate determining step.

The following is a mechanism which would lead to the rate law given in Equation 15. First, there is the rapid equilibrium (Equation 17) between triiodide ion, iodine molecules and iodide ion.

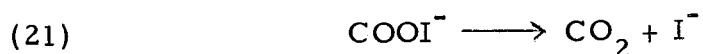
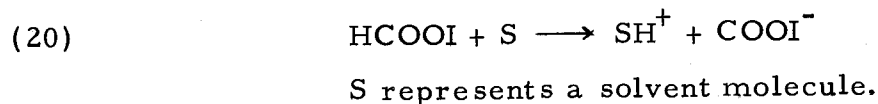
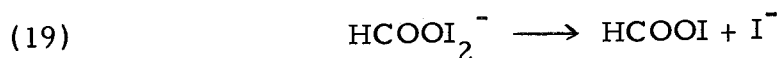


Second, the reaction between iodine molecules and formate ions to form the activated complex in the slow step.



The activated complex then decomposes rapidly by a series of steps into the final products. Perhaps something like the following steps

take place.



The first two steps (Equations 16 and 17) are the essential ones for the observed rate law. If k_1 is the rate constant for the slow step, the rate law would be identical to Equation 14.

The slow step in this mechanism is the reaction between an ion and a neutral molecule. The effect of ionic strength upon such a reaction would be relatively small (27, p. 150-153), while the effect of ionic strength upon a reaction between two ions is relatively large. The fact that there is no appreciable change in rate constant, when ionic strength is increased without increasing the concentration of one of the metal ions (Table 20) supports the idea that at least one of the reactants in the slow step is a neutral molecule.

There are three possible sites of attack for the iodine molecule on the formate ion. These are (1) on the oxygen atoms, (2) on the carbon atom or (3) on the hydrogen atom. Of these three, the attack on the oxygen atoms is the preferred alternative. This seems more likely since, upon its approach to the negative formate

ion, the iodine molecule should become somewhat polarized. The nearer, more positive end of this induced dipole should be attracted more to the more negative oxygen end of the formate ion. Iodine to oxygen bonds occur in iodates, periodates and some other compounds. In fact, hypoiodites of carboxylic acids are known. It is not unreasonable, therefore, to expect iodine-oxygen bonds in the activated complex.

Solvent Effect

The kinetic results show that the value for the rate constant, k , increases by a factor of approximately 10^4 as the solvent is changed from water to DMSO (Table 11). Furthermore, k_1 , the rate constant for the slow step changes even more, since K_d gets smaller as the percent DMSO increases (Table 60). Obviously, the influence of the solvent in the slow step is very great.

This effect is not simply a result of the change in the dielectric constant of the solvent mixture. This is evident since (1) the rate change is too large for the effect of this small dielectric constant change upon a ion-molecule reaction and since (2) the logarithm of the rate constant is not a linear function of the reciprocal of the dielectric constant (Figure 2). The solvent must have a more specific effect, therefore, than simply a dielectric effect.

One of the factors which is involved here is the lack of

ability of the dipolar, aprotic DMSO to solvate the relatively small formate anion by hydrogen bonding (59). Thus, the formate ion becomes less solvated as the solvent is converted from the protic, hydrogen bonding, water to the dipolar, aprotic dimethylsulfoxide. The effective radius of the formate ion is, therefore, decreased as the DMSO content of the solvent increases.

Iodine molecules, on the other hand, are more highly solvated by DMSO than by water due to the polarizability of iodine. This is indicated by the relatively high solubility of iodine in dimethylsulfoxide (38) as compared to its solubility in water, and the fact that iodine forms a complex with DMSO (19, 30, 44). The large increase in the rate constant as the mole fraction of DMSO increases indicates that the desolvation of the formate ion is much more important than the increased solvation of the iodine.

The desolvation of the formate ion, then, has the effect of lowering the effective radius of that ion. It is then more efficient in polarizing the iodine molecule. This then increases the attractive forces between the iodine and formate ion and increases the rate of the slow step in the mechanism.

Ion-pair Formation

The reduction in the reaction rate due to the presence of metal cations has been interpreted as being caused by the formation of

ion-pairs between the metal cation and the formate anion. The fact that the addition of tetraethylammonium cations did not affect the rate indicates that ion-pairing with the tetraethylammonium ion was not extensive. The dissociation constants for the various ion-pairs were calculated on the basis that only the free formate anions react with the iodine molecules but that the various ion-pairs can not react or do so only at a negligible rate.

Ion-pair formation has previously been noted for salts in DMSO by Sears (68) and by Dunnett (21). Dunnett has determined ion-pair formation constants for lithium chloride in DMSO using the approach of Fuoss (27, 28).

The formation of ion-pairs should be aided by (1) a lowering of the dielectric constant for the medium and (2) the decrease in solvation of one or more of the ions. Both of these effects occur in this system, although the dielectric constant effect is relatively small. In fact, the DMSO has a high enough dielectric constant such that dilute solutions of many salts are completely ionized (68). However, the lack of ability to donate a proton for hydrogen bond formation, makes DMSO less capable of solvating formate ions, especially on the more negative oxygen atoms. This increases the tendency of the formate ion to form ion-pairs since it is effectively a smaller ion in DMSO than in water. The dissociation constants for the ion pairs should decrease as the DMSO content of the solvent

increases because of these effects. The results summarized in Table 31 confirm this.

From electrostatic effects one would expect ion-pair formation to become more important as the size of the ion decreases and its charge increases. On this basis we would expect the addition of divalent barium ion to cause a greater slowing effect on the reaction than results from the addition of the univalent cations. Of the alkali metal ions, lithium ion should form ion-pairs to a greater extent than sodium, which in turn should do so more than potassium. This is the order observed in the data.

The assumption that the ion-pair does not react at all with formate ion is not easily justified. Possibly the ion-pair simply reacts much slower and has a smaller dissociation constant than that calculated. It is fairly reasonable to assume that its reaction rate is negligible compared to that of the free formate ion because the negative charge on the formate ion helps polarize the I_2 molecule aiding its attack. Ion-pairs would not do this to a great extent. It also should be noted that the formic acid molecules do not react with iodine. That is if hydrogen ion is added instead of metal ions, a species unreactive to iodine is formed. This might be an indication that the ion-pairs do not react because the charge on the formate ion has been effectively neutralized by the close proximity of the cation.

Temperature Effect

The studies on variation of reaction rate with temperature change have indicated that as the solvent composition is changed from 75% to 94.55% DMSO, the enthalpy of activation has decreased by about 4 kcal/mole and the entropy of activation has decreased by about 8 entropy units. These changes have opposing influences on the rate of the reaction. The enthalpy effect, however, predominates and the reaction is accelerated as the DMSO content of the solvent increases.

This decrease in enthalpy of activation reflects the change in the degree of solvation of the various species involved as the DMSO becomes more dominant in the solvent. Let us compare solvation effects on the original triiodide and formate ions to the effects on the activated complex. The triiodide ion and the activated complex should be similar in some respects. Both should be fairly large and polarizable and both have a negative one charge. The degrees of solvation should be comparable on these two species and solvation effects should roughly cancel out. The formate ion, however, is solvated to a much greater degree by water than by DMSO because of the hydrogen bonding properties of water. It is more stabilized and thus is in a lower energy state when more water is present. Thus the greater the amount of water present, the greater is the

enthalpy of activation.

The change in the entropy of activation as the solvent composition changes can also be explained by the solvent effects. Again the effect of the changes in solvation of the triiodide ion and the activated complex as the solvent changes composition should about cancel. Thus we must consider the effect of the varying degrees of solvation of the formate ion. Let us consider the degree of ordering of solvent molecules about the formate ion in a manner similar to that of Frank and Wen (26). As the mole fraction DMSO increases, solvation decreases and the solvent molecules about the formate ion have more freedom of motion. Thus, there is a greater decrease in solvent ordering in the more aqueous solvent mixture, producing a more positive entropy of activation.

The previous discussion has considered the overall reaction. If we wish to determine the enthalpy and entropy effects for the rate determining step only, we can subtract the entropy and enthalpy changes for the dissociation of the triiodide ion from the overall values. The overall values which would be more meaningful are those involving tetraethylammonium cation, since there is no ion-pairing in this mixture. The results are listed in Table 62.

Table 62. Enthalpies and Entropies of Activation for the Rate Determining Step in Various Solvent Mixtures

Solvent	$\Delta H^\ddagger$, kcal/mole	$\Delta S^\ddagger$, E. U.
94.55% DMSO	11.6	3.3
75.00% DMSO	15.2	5.0
Water (51)	21.4	19.3

The same general trends are still observed as previously. It appears that there are much greater solvent effects on both the entropy and enthalpy of activation in the region where most of the solvent molecules are water as compared to the region where most are DMSO. Again, this indicates that the decrease in solvation of the formate ion by adding DMSO is greater if the water molecules are in the majority, than if DMSO molecules are present in greater quantities. This is reasonable, since the water molecules interact strongly with DMSO molecules by hydrogen bonding. When water predominates, there are excess water molecules to solvate the formate ion. However, when DMSO predominates, most of the water molecules are associated to the DMSO.

Isotope Effect

The deuterium isotope effect upon kinetics is attributed primarily to the difference in zero point energy between the protium and the deuterium compound in the reactant as compared to the

similar difference in the activated complex (78). There is no particular reason for suspecting that the solvent atmosphere should have a large effect upon this difference in zero point energy in a given case, unless the solvent is actually causing a partial breaking of the bond to the hydrogen. The greater the bond breaking, the smaller the difference between the zero point energies. If the bond were completely broken in the activated complex and undisturbed in the reactants we would expect an isotope effect (k_H/k_D) of about seven (78). This value was obtained by Taylor and Halpern (72) in the case of the reaction of basic, aqueous permanganate ion with the formate ion. As a consequence, they suggest a mechanism in which a hydride ion is transferred to the permanganate ion.

Westheimer (77) discusses the isotope effect from the point of view of whether or not the breaking of the bond in question is symmetrical. If it is symmetrical, then the atom in the middle will have lost all of its vibrational energy in the transition state and the isotope effect will be the maximum. If the bond breaking is not symmetrical, then a smaller isotope effect is observed.

In our case, the isotope effect is much less than seven, but it is still large enough to indicate that the breaking of the carbon to hydrogen bond is occurring in the activated complex. The fact that it is less than seven indicates an asymmetrical bond breakage of the carbon-hydrogen bond.

Our isotope effect is about the same as the value of 2.7 that was found by Halpern and Taylor (31, 72) for the oxidation of formate ion by aqueous Tl^{+3} , Hg^{2+} or Hg_2^{2+} ions. In these cases the oxidizing agent undoubtedly attacks the oxygen end of the formate ion. The breaking of the carbon to hydrogen bond in that case, must be assisted by water molecules attacking the hydrogen end of the molecule. This result can be contrasted to the result of their study of the permanganate oxidation of formate (31, 75) ion in which the hydrogen is attacked by the oxidizing agent and they obtain a value of $k_{\text{H}}/k_{\text{D}}$ of about seven.

By inference, our results indicate that the attack of the iodine molecule is on the oxygen end of the formate ion as opposed to the hydrogen end. The breaking of the carbon to hydrogen bond then must be assisted by solvent molecules. The variation in isotope effect as the solvent composition changes reflects the variation in attractive forces between predominantly water molecules attacking the formate hydrogen to predominantly DMSO molecules doing the attacking. There is no question as to the ability of DMSO molecules to attack and solvate protons since it is a basic medium (5, 70) and causes the ionization of acids by solvation of protons (45).

The transition state in the reaction of iodine with formate ion then seems to be one in which an iodine molecule is attacking the

oxygen end of the formate ion. The iodine molecule is undoubtedly polarized by the presence of the negative formate ion. As the iodine molecule approaches, the charge on the formate ion is in effect partially neutralized. This weakens the carbon-hydrogen bonds and makes the hydrogen ions more susceptible to removal by solvent molecules.

SUMMARY

The iodine-formate reaction has the same stoichiometry and obeys the same rate law in DMSO-water mixtures as it does in water. The overall reaction is about 10^4 times greater in DMSO than it is in water. The logarithm of the overall rate constant is very nearly a linear function of the mole fraction of DMSO. The enhancement of the rate by DMSO must be due primarily to more specific effects than the decrease in dielectric constants. Water molecules can solvate formate ions by hydrogen bonding; DMSO molecules can not. As a consequence, the greater the fraction of water molecules present in the solvent, the greater the degree of solvation of the formate ion. The desolvation of the formate ion leads to an enhanced tendency to form ion-pairs with metal cations. A decrease in both the enthalpy and entropy of activation of the iodine-formate reaction is observed as the % DMSO increases. This is also, probably, a result of the desolvation of the formate anion. Kinetic isotope effect studies yield a value of k_H/k_D of from two to four depending on the solvent composition.

It is postulated that the slow step in the mechanism is an attack of a neutral iodine molecule on the formate ion. The deuterioformate studies suggest that the iodine attacks the oxygen side of the formate ion and that solvent molecules are helping to break the carbon to

hydrogen bond in the activated complex. The reaction then proceeds faster in DMSO than in water because the formate ion becomes more susceptible to attack by iodine molecules since it is solvated less strongly by the aprotic solvent. The iodine molecule is somewhat polarized as it approaches the negative formate ion. The induced dipole on the iodine helps to neutralize the charge on the formate ion. This results in a weakening of the carbon-hydrogen bond in the activated complex. The solvent molecules then are better able to remove the proton, because the carbon to hydrogen bond is weaker.

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APPENDICES

APPENDIX I

Derivation of Equation Used for Runs
Involving Low Concentrations of Formate Ion

Assume the rate law,

$$(1) \quad -\frac{d[\Sigma I_2]}{dt} = k \frac{[HCOO^-][\Sigma I_2]}{[I^-]}$$

If the concentrations of the formate and iodide ions are high compared to that of iodine, then one can assume that only the iodine concentration changes during the course of a run. Under those conditions, Equation 1 is a normal first order rate law. Integration of this rate law yields,

$$(2) \quad \ln [\Sigma I_2] = -\frac{k[HCOO^-]}{[I^-]} t + C.$$

Alternatively,

$$(3) \quad \log [\Sigma I_2] = -\frac{k[HCOO^-]t}{2.303 [I^-]} + \log I_{oo}.$$

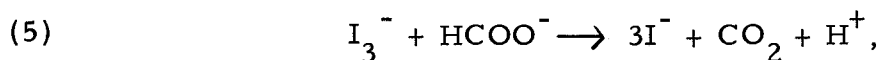
where I_{oo} is the original concentration of I_2 . Since the $[\Sigma I_2]$ is directly proportional to its absorbancy, Equation 3 becomes

$$(4) \quad \log A = -\frac{k[HCOO^-]t}{2.303 [I^-]} + \log A_o$$

where A and A_o are the absorbancies at time t and time

zero, respectively. One then simply plots $\log A$ versus time. The slope of this straight line is $-\frac{k[\text{HCOO}^-]}{2.303[\text{I}^-]}$. One can, then, easily calculate the value of k . If, however, the original concentration is only 10 to 20 times as great as that of iodine, one can no longer consider that the concentration of the formate ion remains constant during the run.

Since the stoichiometry of the reaction is



one knows that, at any given time, the concentrations of free iodine and of formate ions have been reduced the same amount since the beginning of the run. Specifically, at the time when the total concentration of free iodine is given by I , the concentration of formate ion is $F_{\text{oo}} - (I_{\text{oo}} - I)$, where F_{oo} is the original concentration of formate ion.

If we then let $a = F_{\text{oo}}/I_{\text{oo}}$, the concentration of formate ion at time t becomes $(a-1)I_{\text{oo}} + I$, or $b + I$ if $b = (a-1)I_{\text{oo}}$, where I is the total concentration of free iodine at time t .

Our differential Equation 1 now becomes

$$(5) \quad -\frac{dI}{dt} = k'(b+I)I$$

or

$$(6) \quad -\frac{dI}{bI+I^2} = k'dt$$

where $k' = k/[I^-]$.

When one integrates Equation 6 from time zero to time t , one obtains

$$(7) \quad \ln \left(\frac{b+I}{I} \right) = + bk't + c$$

where C is $\ln \left(\frac{b+I_{oo}}{I_{oo}} \right)$. Since $I = \left(\frac{I}{I_{oo}} \right) I_{oo} = \frac{A}{A_o} I_{oo}$

Equation 7 becomes

$$(8) \quad \log \{ (a-1)(A_o/A) + 1 \} = \frac{bk't}{2.303} + C.$$

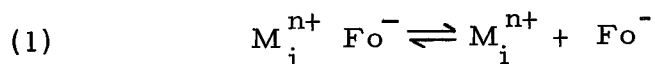
If one then should plot $\log \{ (a-1)(A_o/A) + 1 \}$ versus t , one should obtain a straight line of slope, $S = \frac{bk'}{2.303}$. By substituting back, one obtains for k ,

$$(9) \quad k = \frac{2.303 [I^-] S}{F_{oo} - I_{oo}}$$

APPENDIX II

Derivation of Formulas Used to Calculate
Ion-Pair Dissociation Constants

If one assumes that each of the cations present in the reaction mixture participates in ion-pair formation with the formate ions present to a degree characteristic of the cation, then for each cation there would be an equilibrium of the form,



where Fo^- represents formate ions. The ion-pair dissociation constant, neglecting activity coefficients, would then be

$$(2) \quad K_i = \frac{[M_i^{n+}] [\text{Fo}^-]}{[M_i^{n+} \text{ Fo}^-]}$$

Solving for the concentration of the ion-pair, we obtain

$$(3) \quad [M_i^{n+} \text{ Fo}^-] = \frac{[M_i^{n+}] [\text{Fo}^-]}{K_i}$$

The total concentration of formates (Fo_T) in the system would then be

$$(4) \quad \text{Fo}_T = [\text{Fo}^-] + \sum [M_i^{n+} \text{ Fo}^-]$$

$$(5) \quad \text{Fo}_T = [\text{Fo}^-] \left(1 + \sum \frac{[M_i^{n+}]}{K_i} \right)$$

The total concentration of each of the metal ions (M_{iT}) is

$$(7) \quad [M_i^{n+}] = \frac{M_{iT} K_i}{K_i + [Fo^-]}$$

Substituting in (4), we obtain

$$(8) \quad \frac{Fo_T}{[Fo^-]} - 1 = \sum \frac{M_{iT}}{K_i + [Fo^-]}$$

And since the observed rate is proportional to the concentration of the formate ion, $\frac{k_o}{k} = \frac{Fo_T}{[Fo^-]}$, Equation 7 now becomes

$$(9) \quad \frac{k_o}{k} - 1 = \sum \frac{M_{iT}}{K_i + [Fo^-]}$$

In the cases (1) of a single cation (M) present, or of tetraethylammonium cation and one other cation, we obtain

$$(10) \quad \frac{k_o - k}{k} = \frac{M_T}{K_M + [Fo^-]}$$

and

$$(11) \quad K_M = M_T \left(\frac{k}{k_o - k} \right) + \frac{k}{k_o} Fo_T$$

If we have two cations present, for instance, potassium (K) and lithium (Li), Equation 8 becomes

$$(12) \quad \frac{k_o}{k} - 1 = \frac{K_T}{K_K + [Fo^-]} + \frac{Li_T}{K_{Li} + [Fo^-]}$$

and

$$(13) \quad K_{Li} = \frac{Li_T}{a} - \frac{k}{k_o} Fo_T$$

where

$$(14) \quad a = \frac{k_o}{k} - 1 - \frac{K_T}{K_K + (k/k_o)Fo_T}$$

Formulas 11 and 13 were used in calculating the ion-pair dissociation constants from the kinetic data.