

(2.303/t) $\log(a - x_0)/(a - x)$, and were generally reproducible to $\pm 2\%$.

Enthalpies and entropies of activation were calculated from the expression,⁵⁵ $k_1 = kT/h(e^{-\Delta H^\ddagger/RT})(e^{\Delta S^\ddagger/R})$. A plot of $\log k_1/T$ vs.

(55) F. W. Cagle and H. Eyring, *J. Am. Chem. Soc.*, **73**, 5628 (1951).

$1/T$ was made, and the slope of the best visual straight line (three points) were used to calculate ΔH^\ddagger . Entropies of activation were calculated at all three temperatures and the values averaged; variations between extremes did not exceed 0.1 eu. Relative free energies of activation at 298.16°K were calculated from the relationship, $\Delta F^\ddagger - \Delta F^\ddagger_{\text{H}} = RT \ln(k_1/k_{1\text{H}})$.

Proton Transfers in Dipolar Aprotic Solvents. IV. Solvent Effects on the Rates of Proton Transfers Involving Hydrocarbons

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Abstract: The rates and equilibria of several acid–base reactions involving hydrocarbons have been measured in DMSO solution. The rates of the reactions and Brønsted correlations of the data are compared with similar data for methanol solution reactions. It is concluded that the rates of proton transfer reactions in DMSO solution are greater than those for reactions with the same equilibrium constant in methanol solution. The faster rates are attributed to two factors. (1) In methanol solution, oxygen bases, such as methoxide ion, must be partially desolvated before they can accept a proton from a hydrocarbon acid. (2) The slopes of the Brønsted relationships for reactions in DMSO undergo change from zero to unity in a narrower range of strength of the donor to acceptor than they do in methanol. This indicates that the actual proton transfer step can take place faster in DMSO than in methanol, and the behavior is attributed to solvent reorganization contributions to the free energy of activation.

Although it has generally been found that the proton transfers between oxygen or nitrogen acids and bases take place at diffusion-controlled rates,^{1,2} the situation is often entirely different for carbon acids or bases. For example, the carbon protonation of trifluoroacetylacetonate by hydronium ion occurs with a rate constant of $7.5 \times 10^2 M^{-1} \text{sec}^{-1}$, and the analogous protonation of nitromethyl anion has a rate constant of $6.8 \times 10^2 M^{-1} \text{sec}^{-1}$ in aqueous solutions.¹ For some proton transfers to strongly basic carbanions from alcohols in DMSO solution, however, a variety of studies^{3–5} indicate diffusion-controlled rates.

In order to provide data concerning the sources of the slow rates of reactions of carbon acids in hydroxylic solvents and to investigate the relationship between changes in rates and equilibria resulting from changes in solvent, we have initiated several studies of the reactions of carbon acids in DMSO solution. In a separate series of papers⁶ we have reported the measurements of equilibrium constants, and in the present series of papers⁷ we have already reported the rates of reactions of triphenylmethane with alkoxides and dimethyl ion and some preliminary results of a study of the proton transfer from 9-methylfluorene to 4,5-methylenephenthryl anion.

(1) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

(2) E. Grunwald, *Progr. Phys. Org. Chem.*, **3**, 317 (1965).

(3) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(4) D. J. Cram, F. Willey, H. P. Fischer, and D. A. Scott, *J. Am. Chem. Soc.*, **86**, 5370 (1964), and earlier references cited there.

(5) A. Schreisheim and C. A. Rowe, *Tetrahedron Letters*, 405 (1962); S. Bank, C. A. Rowe, and A. Schreisheim, *J. Am. Chem. Soc.*, **85**, 2115 (1963).

(6) C. D. Ritchie and R. E. Uschold, *ibid.*, **90**, 2821 (1968). This paper contains references to earlier papers.

(7) C. D. Ritchie and R. E. Uschold, *ibid.*, **89**, 2960 (1967); **89**, 1730 (1967).

In the present paper we report the results of studies of the rates of reactions of a series of benzoate ions with fluoradene and 9-carbomethoxyfluorene and of several fluorenyl-type anions with 9-methylfluorene.

Results

All of the reactions reported here have been studied by the stop-flow technique using spectrophotometric detection.⁸ The general techniques have been detailed previously,^{7,8} and are summarized in the Experimental Section.

Rate constants for the hydrocarbon acid–hydrocarbon base reactions are reported in Table I, and those for other types of acids and bases are in Table II. Some isotope effects which have been measured are included in the tables.

The rates of the reactions were measured in only one direction, and the rate constants for the reverse direction were calculated from the known equilibrium constants for the reactions.⁶

The rate constants obtained in this study are not of high precision because of the sensitivity of reactants or products to various impurities, primarily oxygen, and because of the rapidity of the reactions. We estimate a precision and accuracy of *ca.* $\pm 20\%$ for the rate constants and of $\pm 50\%$ for the isotope ratios, $k_{\text{H}}/k_{\text{D}}$.

In addition to the reactions reported in Tables I and II, investigations of the systems shown in Table III have revealed that these reactions occur at rates too great to follow on the stop-flow apparatus. From a conservative estimate of *ca.* 5 msec for mixing time⁸ and observations on dilute solutions, we can confidently

(8) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).

Table I. Hydrocarbon Acid-Hydrocarbon Base Reactions in DMSO Solution at 25°

Acid	Base anion	$k_f^a \times 10^{-2}$	$k_r^a \times 10^{-2}$
Fluorene	9-Methylfluorenyl	2.7	16*
4,5-Methylenepheneanthrene ^{b,c}	9-Methylfluorenyl	7.0	14*
9-Phenylfluorene	9-Methylfluorenyl	1.7*	0.001
Triphenylmethane ^d	Dimsyl	80*	0.0013

^a Rate constants are in units of $M^{-1} \text{sec}^{-1}$. The rate constant actually measured is indicated by an asterisk; the reverse rate constant was calculated from the known equilibrium constant for the reaction. ^b These rates were reported in a preliminary communication (see ref 7). ^c $k_H/k_D = 4.4$. ^d $k_H/k_D = 4.7$, data from ref 7.

Table II. Reactions of *meta*- and *para*-Substituted Benzoate Ions with Hydrocarbon Acids in DMSO Solution at 25°

Benzoate substituent	$k_f^a \times 10^{-4}$	$k_r^a \times 10^{-3}$	k_H/k_D
A. Reactions with Fluoradene			
<i>p</i> -Chloro	2.8	70.	...
Hydrogen	5.1	16.	3.2
<i>p</i> -Ethoxy	9.0	9.0	...
<i>p</i> -Hydroxy	11.	6.5	3.0
<i>p</i> -Amino	24.	1.5	4.6
B. Reactions with 9-Carbomethoxyfluorene			
<i>p</i> -Chloro	1.6	25	...
Hydrogen	3.8	8.0	3.2
<i>p</i> -Ethoxy	6.4	4.0	...
<i>p</i> -Hydroxy	12	3.8	...
<i>p</i> -Amino	16	0.64	3.1

^a Rate constants in units of $M^{-1} \text{sec}^{-1}$.

Table III. Reactions with Rate Constants Greater Than $5 \times 10^6 M^{-1} \text{sec}^{-1}$ in DMSO Solution at 25°

Acid	Base anion	Log K_{eq}^a
Acetylacetone (enol?)	9-Methylfluorenyl	6.3
Benzoic acid	9-Methylfluorenyl	8.7
9-Carbomethoxyfluorene	9-Methylfluorenyl	9.4
Fluorene	Dimsyl	12.0
9-Methylfluorene	Dimsyl	12.8
9-Phenylfluorene	Dimsyl	16.1

^a Equilibrium constant for the acid-base reaction calculated from the measured pK 's of the acids. See ref 6.

set lower limits of $5 \times 10^6 M^{-1} \text{sec}^{-1}$ on the second-order rate constants for these reactions.

In order to substantiate the results of the competition experiments which we have previously reported,⁹ we have attempted to study the rate of the reaction of nitromethane with 9-methylfluorenyl anion in DMSO solution. Using an excess of nitromethane, the disappearance of 9-methylfluorenyl anion follows pseudo-first-order kinetics, but the second-order rate constants obtained decrease with increasing concentration of nitromethane. An increase in concentration of nitromethane from $7.5 \times 10^{-3} M$ to $7.5 \times 10^{-2} M$ results in a decrease in the calculated second-order rate constant from 2.2×10^3 to $8.6 \times 10^2 M^{-1} \text{sec}^{-1}$. It also appears that the isotope effect on the reaction increases with increasing concentration of nitromethane. At $1.5 \times 10^{-2} M$ CD_3NO_2 , we find $k_H/k_D = 1.9$, and at $7.6 \times 10^{-2} M$, k_H/k_D is 4.1. We plan to investigate this reaction further, but we would like to note here that all attempts to study the proton transfer reactions of nitro compounds in DMSO have lead to observations of unusual kinetics.

(9) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **86**, 4488 (1964).

Experimental Section

Materials. The purification of solvent,⁸ preparations of dimethylcesium solutions,⁷ and the source and purification of the compounds used in this study⁸ have been described in earlier papers. Potassium salts of the substituted benzoic acids were prepared by titration of the acids to a potentiometric end point with potassium hydroxide in aqueous methanol. After evaporation of the solvent under vacuum, the salts were recrystallized from 1-propanol and dried in a vacuum desiccator.

Methods. All operations described below were performed under an atmosphere of purified argon.⁸ Transfers of solutions were made with gas-tight syringes.

The reactions of hydrocarbon acids with hydrocarbon bases are carried out as follows. The more basic carbanion is generated in solution by adding an equivalent amount of either dimethylcesium or potassium *t*-butoxide to a solution of the hydrocarbon in DMSO. Generation of the carbanion with either base gave the same results. The carbanion solutions were generally $<10^{-4} M$ concentration. The carbanion solution is mixed in the stop-flow apparatus with a more concentrated solution of the other hydrocarbon acid. The hydrocarbon acid solution was always at least ten times more concentrated than the carbanion solution, and pseudo-first-order kinetics were always observed. The reactions were followed both by disappearance of reactants and, in separate runs, by appearance of products. Runs utilizing different concentrations of the hydrocarbon acid served to show that the reactions were second order over-all.

Equilibrium constants for the reactions, calculated from the "infinity" readings, were in good agreement with those calculated from the reported⁶ pK 's of the acids. Reverse rate constants are evaluated from the measured forward rate constants and the equilibrium constants.

The reactions of the hydrocarbon acids with benzoate ions were studied by mixing solutions of the benzoate ions with solutions of the hydrocarbons in the stop-flow apparatus. The reactions were followed by observing the appearance of the carbanion. The benzoate ion concentrations ($ca. 10^{-4}$ to $10^{-3} M$) were always in excess of the hydrocarbon concentration so that pseudo-first-order kinetics were observed.

The isotope effects on the reaction of 9-methylfluorene with 4,5-methylenepheneanthryl anion was established in a straightforward manner by the use of 9-methylfluorene-9-*d*.

It is believed, however, that fluoradene 9-*d* and 9-carbomethoxyfluorene-9-*d* exchange with the small amount of water ($<10^{-3} M$) present in the purified solvent. The isotope exchange was established by observing the infrared spectrum of a $5 \times 10^{-2} M$ solution of 9-carbomethoxyfluorene in DMSO to which had been added $5 \times 10^{-2} M$ D_2O . The infrared spectrum of the mixture showed a weak C-D band at 4.7μ , and the D_2O band at 4.97μ was quite different from that of D_2O in DMSO and almost identical with that of an equimolar mixture of H_2O and D_2O in DMSO. This experiment was carried out after it was found that the reaction of 9-carbomethoxyfluorene-9-*d* ($ca. 10^{-3} M$) with benzoate ion occurred at exactly the same rate as did the reaction of the hydrogen compound. We may note in passing that we have found that the exposure of fluoradene-9-*d* to the atmosphere for several hours results in the loss of $ca. 20\%$ of the deuterium.

In order to measure the isotope effects on the above reactions, we resorted to the subterfuge of adding $10^{-3} M$ D_2O to the solution of the deuterated hydrocarbon. It was found that the addition of $10^{-3} M$ H_2O to the solution of the ordinary hydrocarbon had no effect on the rates of reaction with any of the benzoates.⁷ Since the amount of water in the solvent is less than $10^{-3} M$, the addition of $10^{-3} M$ D_2O should prevent any exchange of the deuterated hydrocarbon in solution, and we have observed the isotope effects reported in Table II.

Discussion

The pK 's of the various acids used in the present study have been reported in separate papers.⁶ Brønsted plots of the reactions of the substituted benzoate ions with fluoradene and with 9-carbomethoxyfluorene are shown in Figure 1. The Brønsted slopes are 0.40 for both reactions.

The reactions of 9-methylfluorenyl anion with the three hydrocarbon acids appear to be subject to an appreciable steric effect. The rate of reaction of 9-phenylfluorene, the strongest acid, is actually slightly less than those of 4,5-methylenephenanthrene and fluorene. Fluorene and 4,5-methylenephenanthrene show the expected order of reactivity with the slightly more acidic 4,5-methylenephenanthrene reacting fastest. It is somewhat surprising to find these reactions of very bulky acids with a bulky base occurring at such high rates. In ether solutions,¹⁰ reactions between fluorene-type acids and bases occur much more slowly, probably because of ion pairing. Unfortunately, it has not, as yet, been possible to measure the rates of such reactions in hydroxylic solvents.

Streitwieser¹¹ has reported the rates of reactions of a number of fluorene-type hydrocarbons with methoxide ion in methanol solution. These rates were followed by hydrogen-tritium exchange of the tritiated hydrocarbons at various temperatures and have been adjusted to a common temperature of 45° by use of the measured energies of activation.

We have recently pointed out that the pK 's of acids such as fluorene and triphenylmethane can be estimated for methanol solution if they are known for DMSO solution.⁶ For acids of this type, whose conjugate bases are highly colored, the pK 's in methanol are expected to be *ca.* 6.5 units higher than the values in DMSO.

With this information, we can estimate rate constants for the reactions of methanol with the carbanions and construct Brønsted plots for the forward and reverse reactions. The rate constants estimated in this way are uncertain due to isotope effects in the detritiation measurements and due to any uncertainties in the estimated pK values. The estimates are probably good to within a factor of 10, however. Rate constants are shown in Table IV.

The first point of interest in the data of Table IV is that the rate constants for protonation of the hydrocarbon anions are in the range of $10^5 M^{-1} \text{sec}^{-1}$, with the exception of triphenylmethyl anion. These rate constants for reactions with equilibrium constants of *ca.* 10^8 are of the same magnitude as those for the protonation of fluoradene by *p*-chlorobenzoic acid, where the equilibrium constant is only *ca.* 30, in DMSO solution. For reactions with similar equilibrium constants in the two solvents, the rate of proton transfer is much faster in DMSO solution.

In order to discuss the data in Tables II and IV fully, it is convenient to construct Brønsted plots of the type suggested by Eigen,¹ where the rate constants for both forward and reverse reactions are plotted against the equilibrium constants for the reactions. Such a plot,

(10) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **89**, 2764 (1967).

(11) A. Streitwieser, A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89**, 693 (1967).

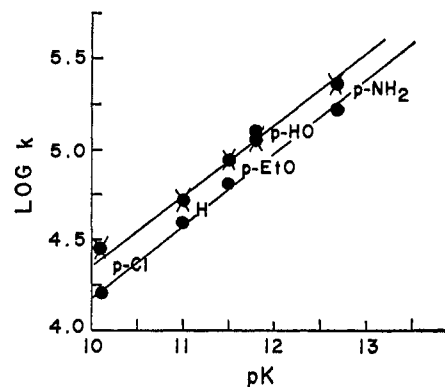


Figure 1. Brønsted plot of rates of reactions of substituted benzoate ions with 9-carbomethoxyfluorene (●) and fluoradene (⊗).

for reactions in both methanol and DMSO, is shown in Figure 2. Two aspects of this plot for methanol solutions have been confirmed by Streitwieser.¹² It has been found that the Brønsted plot shows curvature, with a slope of *ca.* 0.4 around fluorene and *ca.* 0.9 around triphenylmethane. As predicted⁶ on the basis of a

Table IV. Estimated^a Rate and Equilibrium Constants for the Reactions^b

$$\text{CH}_3\text{O}^- + \text{RH} \xrightleftharpoons[k_r]{k_f} \text{CH}_3\text{OH} + \text{R}^-$$

RH	$k_f^c \times 10^4$	$k_r^c \times 10^{-5}$	pK_{eq}^d
Fluorene	4.32	2.1	8.7
9-Methylfluorene	1.12	0.09	7.9
9-Ethylfluorene ^e	0.78	0.05	8.8
3,4-Benzofluorene ^e	113	0.18	6.2
4,5-Methylenephenanthrene	8.35	1.3	8.2
2-Bromofluorene ^e	95	1.5	7.2
9-Phenylfluorene	170	0.008	4.6
9-Benzylfluorene ^e	3.1	0.2	7.8
Triphenylmethane	1.0×10^{-5}	10^3	17.0

^a Rate and equilibrium constants are estimated as described in text. ^b In methanol at 45°, from ref 11. ^c Rate constants are in units of $M^{-1} \text{sec}^{-1}$. The reverse rate constant, k_r , is a second-order constant since the pK of methanol has been taken as 18.3, which includes the concentration of methanol.⁸ ^d Estimated negative log of the equilibrium constant for the reaction, including the concentration of methanol. ^e These pK values in DMSO are taken from the work of K. Bowden and A. F. Cockerill, *Chem. Commun.*, 989 (1967), and are adjusted to $pK = 20.5$ for fluorene. See ref 6.

Brønsted slope approaching unity and a reverse rate close to diffusion controlled, the reaction of triphenylmethane with methoxide has been found¹² to show an isotope effect (at 100°), $k_D/k_T = 1.3$ ($k_H/k_D \approx 2$), which is much smaller than that for fluorene (at 25°), $k_D/k_T = 2.2$ ($k_H/k_D \approx 6$).

In methanol solution, as shown in Figure 2, the rates of reaction of methanol with carbanions become diffusion controlled only when the ΔpK is greater than 18. The rates of reaction of methoxide with hydrocarbons at the negative end of the ΔpK scale (*i.e.*, hydrocarbons more acidic than methanol) appear to be leveling out considerably below the expected value for diffusion control. Eigen¹ has remarked on similar behavior for the reaction of acetylacetone in aqueous solution. In terms of the three-step mechanism for proton-transfer

(12) A. Streitwieser, private communication, Oct 1967. We are grateful to Professor Streitwieser for informing us of these results prior to publication.

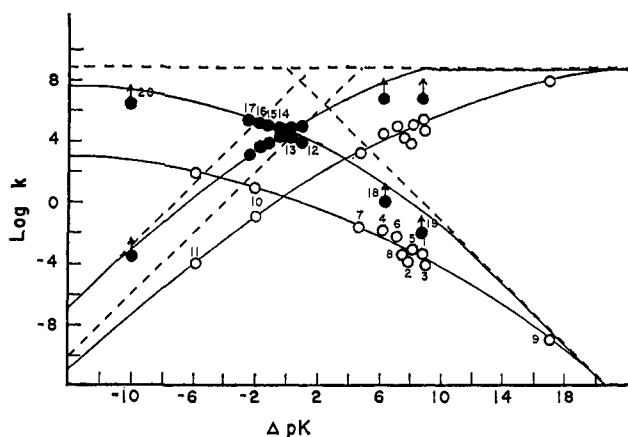
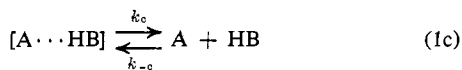
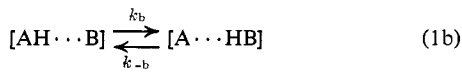
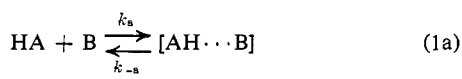


Figure 2. Extended plot of forward and reverse rates of reactions of hydrocarbons with anionic oxygen bases in methanol (open circles) and in DMSO (closed circles). Points 1–9 are from data in Table IV; points 12–17 are from data in Table II; and points 18–20 from Table III. Point 10 is for the reaction of 9-trifluoromethylfluorene in methanol¹⁴ which has an estimated pK of ca. 16. Point 11 is for the reaction of nitromethane in methanol, with an estimated pK of ca. 12.

reactions¹



the behavior is attributed to the instability of the encounter complex $[\text{AH} \cdots \text{B}]$ when AH is a poor hydrogen bond donor and B is strongly solvated by hydrogen bonding with solvent. Thus, even if k_{-a} is very large, the unfavorable equilibrium constant for step 1a keeps k_a small. Similar factors have been discussed by Ogg and Polanyi¹³ and by Moelwyn-Hughes¹⁴ for the S_N2 reactions of hydroxide ion, and by Caldin¹⁵ for other types of reactions. Polanyi phrased it that: "The reason for this repulsion between the ions at moderate distances in solution is that their nearer approach requires the removal of part of the solvation shells, with a corresponding increase in the potential energy." We¹⁶ have recently discussed the pertinence of this concept to the mechanism of the reaction of hydrogen molecule with aqueous hydroxide solutions, which is a deceptively simple appearing example of a proton transfer reaction.

In DMSO solution, the proton transfer reactions of hydrocarbons approach diffusion-controlled limits, in both directions, at much smaller values of ΔpK than in methanol. For negative values of ΔpK , the rates do not level out at values far below diffusion control as they do in methanol. This, of course, is consistent with the concept of desolvation discussed above. In DMSO, anions are not hydrogen bonded to solvent and apparently do not need to lose the energy of solvation in order to accept a proton. This could arise because of small solvation energies of the anions in

DMSO relative to those in hydroxylic solvents or because the anions can interact with the hydrocarbon acids nearly as strongly as with solvent.

The fact that the protonation of carbanions in DMSO approaches diffusion control at lower values of ΔpK than in methanol also requires some explanation. There is no reason to expect k_a for this process to be greater in DMSO than in methanol, and, in fact, the reverse might be expected since DMSO appears to be a better hydrogen bond acceptor than is methanol, and step 1a would then be expected to have a smaller equilibrium constant in DMSO than in methanol. The indication, then, is that there is a solvent effect on step 1b. Consideration of the relative rates of reactions with the same value of ΔpK in the two solvents leads to the same conclusions.

The origin of the solvent effect on step 1b is suggested to be due to differences in solvent reorganization energies in the two media. This concept was first suggested for proton transfer reactions by Caldin¹⁵ and is quite similar to the concept applied to discussions of outer sphere electron-transfer processes in solution.¹⁷ The locations of solvent molecules at equilibrium with the species $[\text{AH} \cdots \text{B}]$ and those with $[\text{A} \cdots \text{HB}]$ are, most likely, quite different. Energy to reorganize the solvent must be supplied in exactly the same way that it has been assumed that energy must be supplied to effect geometrical changes of the reacting molecules themselves.^{17,18} It is important to realize that an ion in solution cannot be discussed without a consideration of the "solvating" molecules associated with it. The nature of an ion in solution is entirely different from that in the gas phase, and an implicit extension of this obvious fact is that ions in two different solvents are entirely different.

The amount of energy required to reorganize DMSO during the transition from $[\text{AH} \cdots \text{B}]$ to $[\text{A} \cdots \text{HB}]$ is expected to be less than that for methanol because of the importance of oriented hydrogen bonds in methanol solution.⁸ That is, in methanol, the solvent around the hydrocarbon molecule, which is undoubtedly hydrogen bonded to other solvent molecules, must completely rearrange on formation of the carbanion. In even more general terms, the creation or destruction of a very concentrated charge will drastically alter solvent orientation, and if this involves even partial breaking of several hydrogen bonds, we may expect appreciable contributions to the free energy of activation.

Concepts similar to those discussed above have recently been presented in connection with other types of organic reactions. The concept offered by Malinowski and Bruning¹⁹ to explain the slow rate of electron transfer from benzene radical anion to benzene appears to be quite close to the solvent reorientation concept. Cockerill and Saunders²⁰ point out the possible influence of desolvation of hydroxide ion on the rates of E2 eliminations of 2-phenylethyldimethylsulfonium ion in various aqueous DMSO systems.

Acknowledgments. This work was supported by Grants GM-12832 from the U. S. Public Health Service, National Institutes of Health, and GP-5853 from the National Science Foundation.

(13) R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935).
 (14) D. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **A211**, 254 (1952).
 (15) E. F. Caldin, *J. Chem. Soc.*, 3345 (1959).
 (16) C. D. Ritchie and H. F. King, *J. Am. Chem. Soc.*, **90**, 833 (1968).

(17) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).
 (18) See, for example: J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); *J. Am. Chem. Soc.*, **88**, 5525 (1966).
 (19) G. L. Malinowski and W. H. Bruning, *ibid.*, **89**, 5064 (1967).
 (20) A. F. Cockerill and W. H. Saunders, *ibid.*, **89**, 4985 (1967).