Electron Paramagnetic Resonance Studies of the Effects of Solvation on the Electron- and Cation-Transfer Reactions in Ketyls[1]

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Abstract: The effects of solvation on the rate of electron-transfer reactions between ketyls and ketones are investigated. It was found that the strong solvation of the cation by DMF and BMEE drastically retards the rate of the electron transfer. Solvation of anion by alcohol also reduces the reaction rates. The observed solvation effects were discussed in terms of the suggested mechanism of electron-transfer reaction. The exchange of Na^+ cations associated with ketyls was investigated. The exchange rate constants for the free cation and the ion-paired cation ($NaBPh_4$) were estimated. It was found that the cation transfer in the solution of $NaBPh_4$ is cnly effective for the free Na^+ ion. Solvent effects in the cation-transfer reactions were also investigated.

Rapid electron- and cation-transfer reactions involving radical anions have been investigated by epr for the last 15 years.[3–12] Yet the relationships between the reaction rates and the detailed ion-pair and solvation structures have begun to be understood only recently.[9–12] In the earlier studies the effects of ion-pair structures on electron-transfer reaction rates in naphthalenide and anthracenide were investigated.[9,10] It was noted that the rate constants for loose ion pairs are usually $10^8 \sim 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, while the rate constants for tight ion pairs (contact ion pairs) are of the order of $10^6 \sim 10^7\ M^{-1}\ \mathrm{sec}^{-1}$. On the other hand, the rate constants in ketyls were found to be much faster, on the order of $10^8 \sim 5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$, despite the fact that these ion pairs have contact structures.[6] Furthermore, an opposite trend was found for the solvent dependence of the electron-transfer rates between two systems in going from DME to MTHF. It was thought that this difference could be attributed to the polar nature of the carbonyl compound which could facilitate the formation of an intermediate, $Ar_2\dot{C}O^-M^+O{=}CAr_2$, through which electron transfer takes place.

The intermolecular cation-transfer reaction has been studied in a few systems, but not much is known about the details of the cation-transfer process.[6,13,14] When alkali metal salts are added to these solutions both free cations and ion pairs exist. In the present study we have estimated the individual rate constants for both the free cations and the ion pair.

We have investigated the solvent effects on electron- and cation-transfer reactions in sodium fluorenone ketyls (Fl^-Na^+). The major objectives of these studies were, first, to determine in detail how changes in sovation and ion-pair structure affect reaction rates and, second, to attempt a determination of the detailed mechanisms.

To study the effects of solvation, two different types of solvents were chosen: (1) cation-solvating solvents and (2) anion-solvating solvents. Examples of the cation-solvating solvents used are *N,N′*-dimethylformamide (DMF) and bis[2-(2-methoxyethoxy)ethyl] ether (BMEE). We used isopropyl alcohol (*i*-PrOH) as an anion-solvating solvent. In the mixtures of these solvents the fluorenone ketyls form rapid equilibrium mixtures of unsolvated and solvated ion pairs. The details of the solvation process have been investigated in our laboratory.[15,16] It is, therefore, possible to relate the kinetic data with detailed solvation structures.

Experimental Procedures and the Basis of Analysis

Preparation of solutions of radical anions (fluorenone ketyls) and addition of *i*-PrOH, DMF, and BMEE to ethereal solutions have been described elsewhere.[8,15–17] *i*-PrOH, DMF, and BMEE were purified by refluxing with baked molecular sieves followed by distillation. DMF and BMEE were stored together with fluorenone ketyls.

All epr measurements were made on a Varian V-4502 spectrometer. The determination of electron- and cation-transfer reaction rates was made by measuring the increase in line width between the points of extreme slope of the epr spectra after the addition of known amounts of either neutral fluorenone or sodium tetraphenylboride ($NaBPh_4$) to dilute solutions of fluorenone ketyls.

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(1) This work was supported by the grant from the National Foundation.

(2) Taken from a M.S. Thesis submitted by B. F. Wong.

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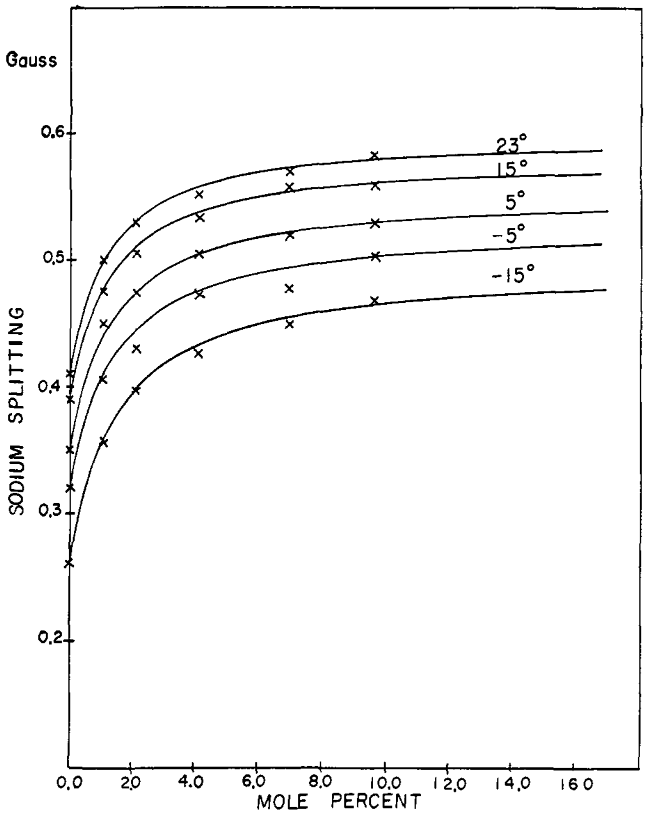

Figure 1. Changes of sodium splittings of sodium fluorenone ketyl upon addition of DMF into THF solution at various temperatures. X's represent experimental points. Curves are predicted by eq 2 using appropriate values of K and a_2.

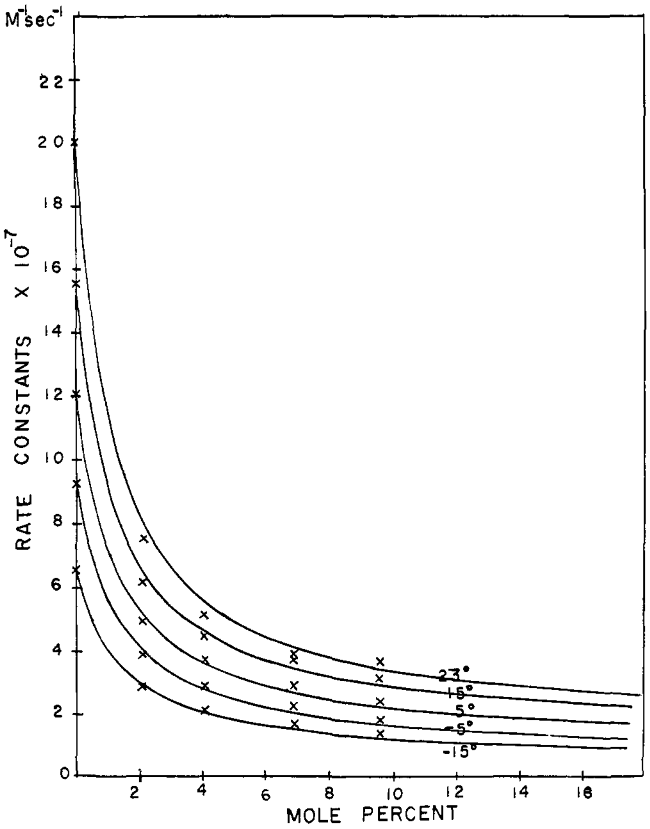

Figure 2. Changes of the rate constants for electron-transfer reactions upon the addition of DMF into THF solution at various temperatures. X's represent experimental values. Curves are predicted ones from eq 3 using f_u and f_s obtained from the data shown in Figure 1.

The line width measurements were made on several peaks which overlapped least with other peaks and were of reasonable intensity. All rate measurements were made in the slow exchange region. The rate constants for electron-transfer reactions were determined by using the well-known formula[3c]

$$k = 1.52 \times 10^7 \Delta He/[\mathrm{R}]\ M^{-1}\ \mathrm{sec}^{-1} \qquad (1)$$

where ΔHe is the increase in the line width in gauss due to the exchange process and [R] is the concentrations of neutral molecules. In the case of cation-transfer reactions, the rate constants were determined by using

$$k' = 2.03 \times 10^7 \Delta He/[\mathrm{M}]\ M^{-1}\ \mathrm{sec}^{-1} \qquad (1')$$

where [M] is the concentration of the added cation. The difference between eq 1 and 1′ is due to the fact that $^1/_4$ of the system goes back to a state with the same sodium nuclear quantum number after cation transfer.[4]

Experimental Results

A. Electron-Transfer Reactions. 1. Electron-Transfer Reactions in Pure THF. The electron-transfer reaction of fluorenone ketyl is first order with respect to fluoroenone ketyl. The rate constant for the electron transfer at 25° is 2.4 × $10^8\ M^{-1}\ \mathrm{sec}^{-1}$ with an activation energy of 4.2 kcal. These values are very similar to those obtained for other ketyls such as benzophenone and xanthone ketyls.[6]

2. Effects of the Addition of DMF. It is known from previous studies that DMF replaces THF and preferably solvates $\mathrm{Na^+}$ ion.[16] Figure 1 shows the change of the sodium splittings (a_{Na}) caused by addition of DMF at different temperatures. The observed changes in splittings were computer fitted using the equilibrium scheme (2) and assuming that the spectra are in the rapid equilibrium region. Here

$$\underset{a_1}{\mathrm{Fl^-Na^+(THF)}_n} + \mathrm{DMF} \rightleftarrows \underset{a_2}{\mathrm{Fl^-Na^+(DMF)(THF)}_{n-1}} + \mathrm{THF} \qquad (2)$$

$$K = \frac{[\mathrm{Fl^-Na^+(DMF)(THF)}_{n-1}][\mathrm{THF}]}{[\mathrm{Fl^-Na^+(THF)}_n][\mathrm{DMF}]} \qquad (2a)$$

$$a_{\mathrm{Na}} = \frac{a_1 + a_2K[\mathrm{DMF}]/[\mathrm{THF}]}{1 + K[\mathrm{DMF}]/[\mathrm{THF}]} \qquad (2b)$$

a_2 and a_1 are the sodium splittings of the DMF solvated and the unsolvated ketyls. It is seen that the observed values are very well fitted by the above solvation scheme. In solutions with low percentage of DMF (<15%) the major species in solution are DMF solvated ion pairs and THF solvated pairs. Figure 2 shows the change of the electron-transfer reaction rate as a function of the percentage of DMF. It is seen that DMF solvation drastically retards the reaction rates. Since the DMF solvated species and the unsolvated species rapidly interconvert the observed overall rate constants are given by

$$k = f_s k_s + f_u k_u \qquad (3)$$

where f_s and f_u are the fractions of the DMF solvated

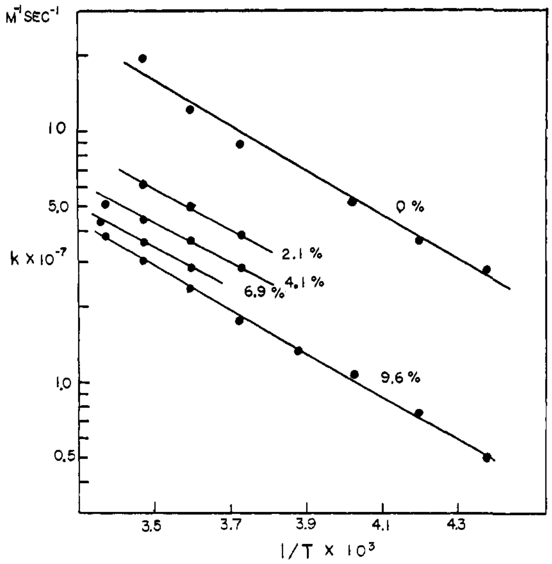

Figure 3. Plots of log k *vs.* $1/T$ for electron-transfer reactions in solutions of different mole per cents of DMF.

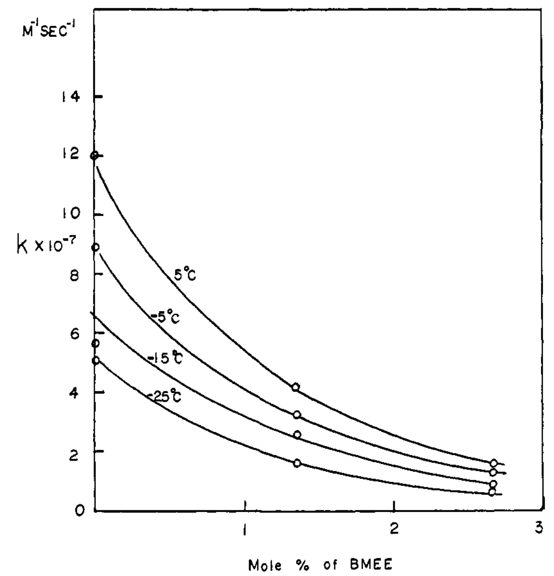

Figure 4. Changes of the rate constants for electron-transfer reactions upon addition of BMEE at various temperatures.

and the unsolvated species, and k_s and k_u are their respective rate constants. The changes in rate constants by DMF solvation were predicted by using eq 3, with f_s and f_u determined from the fits shown in Figure 1, and the observed values of k_u in pure THF and k_s estimated from the rates in the mixtures with high percentage of DMF. The predicted curves agree with the observed ones quite satisfactorily. In Figure 3 log k *vs.* $1/T$ at different percentages of DMF is given. For 0 ~ 10% solutions of DMF the plots give almost identical activation energies, ~4.0 ± 0.3 kcal. This result is reasonable since $k_u \gg k_s$ and the activation energy determined here represents that for k_u. Generally k_s was found to be $\sim 1/15k_u$. Thus the solvation of the cation by one DMF molecule drastically slows down the electron-transfer reaction rate (Table I).

Table I. Values of K, k_u, and k_s Used to Obtain Curves Given in Figures 1 and 2

Temp, °C	K	$k_u \times 10^{-7}$ M^{-1} sec^{-1}	$k_s \times 10^{-7}$ M^{-1} sec^{-1}
23	85	20.0	1.4
15	80	15.5	1.25
+5	75	12.0	0.85
−5	70	9.2	0.53
−15	65	6.5	0.37

3. Effects of BMEE Addition The sodium splitting of fluorenone ketyl is not changed greatly by the addition of BMEE at room temperature but is increased slightly at lower temperatures by the addition of BMEE, indicating that sodium ion is solvated by BMEE. It is also well known that polyethers such as BMEE are good cation-solvating species.[12,18] However, it is not possible to make accurate estimates of the equilibrium constant for solvation since the change of the splitting by the addition of BMEE is very small. The rate constants for the electron-transfer reaction in mixtures of THF and BMEE are given in Figure 4. It is shown that addition of a small amount of BMEE slows the rates drastically. The electron-transfer rate constant for the BMEE solvated ketyl is more than one order of magnitude smaller than that for the ketyl in pure THF. The large decrease of the rate constant by BMEE solvation is remarkably different from the case of naphthalenide studied by Szwarc, *et al.*, where BMEE solvation enhances the rate constant.[12]

4. Effects of the Addition of *i*-PrOH. The solvation of fluorenone ketyls by *i*-PrOH has been investigated in our laboratory.[15] The initial step of solvation is the solvation of the carbonyl oxygen by *i*-PrOH through the hydrogen bonding, but the second step of solvation becomes progressively more important as the percentage of alcohol increases. Under such conditions there are more than two species in solution and the simple analysis by eq 3 is not applicable. Figure 5 shows the change of the electron-transfer reaction rate as a function of *i*-PrOH. The apparent rate constant clearly is decreased by the addition of *i*-PrOH. Our recent studies indicate that in THF–*i*-PrOH mixtures there are three major species: unsolvated ion pairs, monosolvated ion pairs, and doubly solvated ion pairs.[15] When the percentage of alcohol is less than 5%, the concentration of the doubly solvated species is small. The fits to this position of the experimental curves indicate that k_1 (the rate constant for the monosolvated ion pair) is approximately $^1/_3$ of k_u (the rate constant for the unsolvated ion pair). In mixtures of higher alcohol concentration the rate constant decreases further indicating that k_2 (the rate constant for the doubly solvated species) is even slower. The log k *vs.* $1/T$ plots show gradual increase of slopes in the solutions with higher percentage of alcohol. This indicates that the activation energy for the alcohol-solvated ketyl is higher.

B. Cation-Transfer Reactions. 1. Cation-Transfer Reaction in Pure THF. It is known that in solutions of $NaBPh_4$ the free cation, Na^+, and the ion pair Na^+-BPh_4^- exist.[19] The possible cation-transfer reactions

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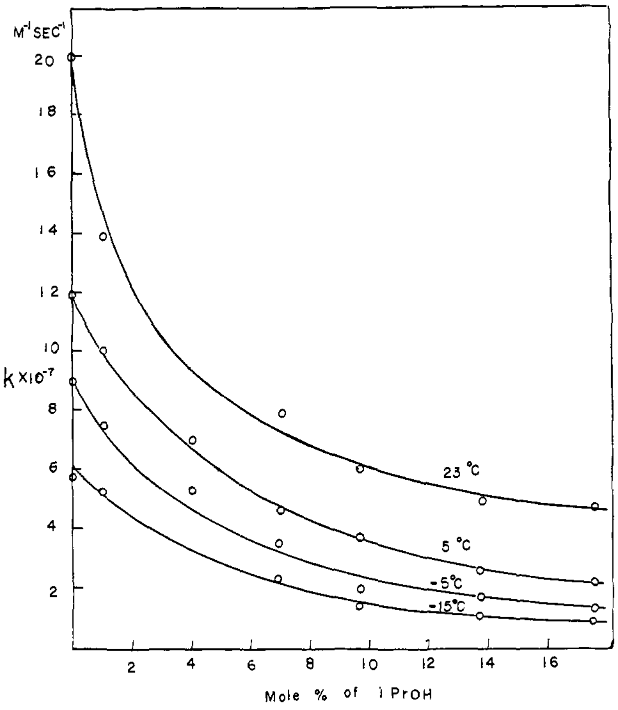


Figure 5. Changes of the constants for electron-transfer reactions upon addition of *i*-PrOH at various temperatures.

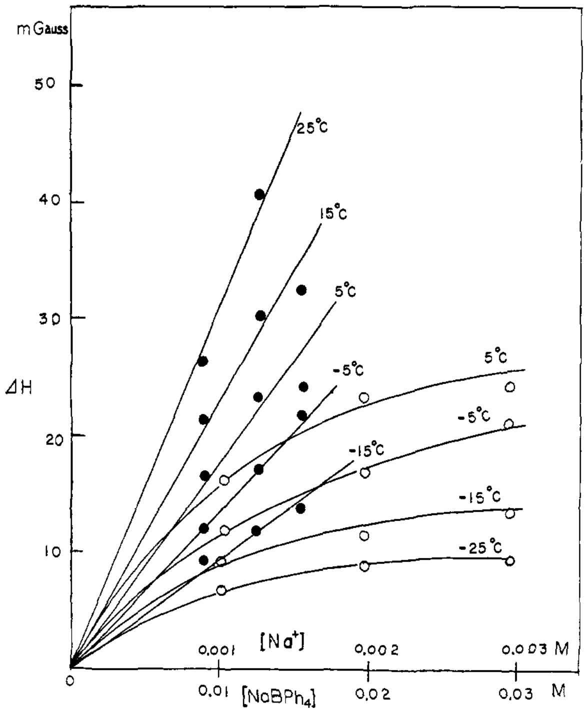


Figure 6. Plots of ΔHe *vs.* [Na$^+$] and [Na$^+$BPh$_4^-$] for cation-transfer sections: (—●—), ΔHe *vs.* [Na$^+$]; (—○—), ΔHe *vs.* [Na$^+$BPh$_4$].

are

$$\mathrm{Fl^-Na^+ + Na'^+ \underset{k_f}{\overset{k_f}{\rightleftharpoons}} Fl^-Na'^+ + Na^+} \qquad \text{(A)}$$

or

$$\mathrm{Fl^-Na^+ + Na'BPh_4 \underset{k_i}{\overset{k_i}{\rightleftharpoons}} Fl^-Na'^+ + NaBPh_4} \qquad \text{(B)}$$

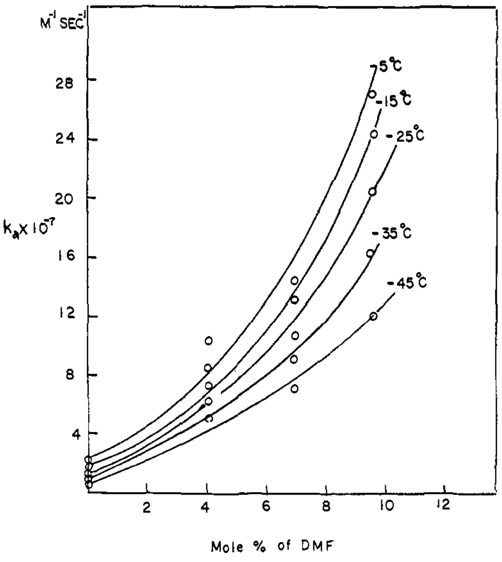


Figure 7. Changes of apparent rate constants for cation-transfer reactions upon addition of DMF at various temperatures. k_a was defined as k_a = rate/[NaBPh$_4$][R], where [R] and [NaBPh$_4$] are the concentrations of fluorenone ketyl and NaBPh$_4$. Measurements were made at [MBPh$_4$] = 4×10^{-3} *M*.

If reaction A is the main reaction, ΔHe, the line broadening due to the exchange process, is not linear with respect to the concentration of NaBPh$_4$. The concentration dependence of ΔHe is given in Figure 6. It clearly shows that ΔHe is not linear with respect to [NaBPh$_4$]. Using the known dissociation constants of NaBPh$_4$, the concentration of Na$^+$ was estimated. The plots of ΔHe against [M$^+$] were found to be approximately linear, although the points are somewhat scattered. Therefore, it is concluded that process A is the main reaction. Our results are different from the case studied by Rutter and Warhurst where the cation exchange rate is linear with respect to the concentration of the added salt.[20] The transfer rate constant for the free cation, k_f, is estimated to be 4×10^8 M^{-1} sec^{-1} at 25°. k_i for ion pair is estimated to be smaller than 10^7 M^{-1} sec^{-1}.

2. Effects of DMF Addition. As shown in Figure 7, very large increases in rates were observed on addition of DMF. From our recent work on ketyls it is known that the addition of DMF greatly exhances the dissociation of the ion pairs.[16] Therefore it is expected that the addition of DMF will enhance the concentration of Na$^+$ ion and the exchange rate. With 10% of DMF added the cation-transfer rate constant approaches that expected for the free cation. We think that the increase of free cation concentration is the main cause of the increase of rate by the addition of DMF.

3. Effects of BMEE Addition. The effects of BMEE addition on the cation-transfer rate were investigated in the range of 0 ~ 5% of BMEE. The cation-transfer rates were not affected much by the addition of BMEE, although the rate seems to decrease slightly at higher percentage of BMEE. Na$^+$ ion is expected to be solvated by BMEE. However, dissociation probably is not increased much by this solvation and this is perhaps the reason for the small change in rate by the addition of BMEE.

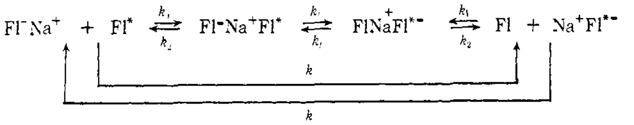
4. Effects of Alcohol Solvation. The effects of alcohol solvation on the overall rate of the cation-transfer

(20) A. W. Rutter and E. Warhurst, *Trans. Faraday Soc.*, **66**, 1866 (1970).

reaction are given in Figure 8. The overall rate increases in the beginning but reaches a maximum at ~7% of *i*-PrOH and then gradually decreases. At this percentage of *i*-PrOH the percentage of monosolvated ion pair, $Ar_2\dot{C}O^-Na^+HOR$, also approaches the maximum. Therefore it appears that the cation-transfer rate for the monosolvated ion pair is faster than for the monosolvated ion pair. However, the concentration of Na^+ in solution may be changed by the addition of *i*-PrOH. Thus it is difficult to determine the effect of alcohol solvation on the cation-transfer rate quantitatively. The gradual decrease of the rate constant at higher concentration of *i*-PrOH seems to indicate that the cation-transfer rate for the doubly solvated ion pair is slower than for the monosolvated ion pair.

Discussion

A. Mechanism of the Electron-Transfer Reaction and the Solvation Effects. The electron-transfer reaction in ketyls is known to proceed as a cation-transfer reaction.[6,21] As mentioned in the introduction ketones are polar molecules and the most plausible mechanism for transfer is through the formation of an intermediate, $Ar_2\dot{C}—O^-Na^+O{=}CAr_2$. If this is the case the reaction is written as



$$Fl^-Na^+ + Fl^* \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fl^-Na^+Fl^* \underset{k_t}{\overset{k_t}{\rightleftarrows}} Fl\overset{+}{Na}Fl^{*-} \underset{k_2}{\overset{k_1}{\leftrightarrows}} Fl + Na^+Fl^{*-}$$

The first step is the formation of an intermediate and the second step is electron transfer in the intermediate. If we assume $k_t \gg k_1, k_2$, the observed rate constant k is given by $1/2k_1$. Then the overall electron transfer is controlled by the rate of formation of the intermediate. The effects of solvation on the transfer rates observed in this study are consistent with this mechanism and lend strong support for it.

In order to make an intermediate complex, neutral fluorenone has to form a complex with the cation, displacing solvent molecules attached to the cation. This becomes more difficult when the cation is already solvated by strong cation-solvating solvents such as DMF and BMEE. Therefore, drastic reductions of the rate constant of electron transfer for DMF and BMEE solvated ketyls are expected from the above mechanisms. In pure solvent the formation of the intermediate is easier when the solvent is less strongly solvated to cation. The solvent dependence of the transfer rate in ketyls is exactly the expected order, $k_{\mathrm{MTHF}} > k_{\mathrm{THP}} > k_{\mathrm{THF}} > k_{\mathrm{DME}}$.[6] The formation of the intermediate is probably not much affected by alcohol solvation. However, the anion is solvated by alcohol and the solvation structure of the anion is different from that of neutral carbonyl molecules. In order to transfer an electron, the solvation structure of both the carbonyl molecules in the transition complex should be similar. This may be achieved by removing solvated alcohol from the anion or by the solvation of the neutral molecule by another alcohol molecule. In either case reorganization of the solvation structure is necessary before the electron can transfer. Thus it is reasonable that the rate constants for electron-transfer reactions are decreased by solvation of the anion by alcohol. The decrease of the rate constants by the anion solvation is somewhat analogous to what was found in the case of nitrobenzene anions by Adams, *et al.*[22]

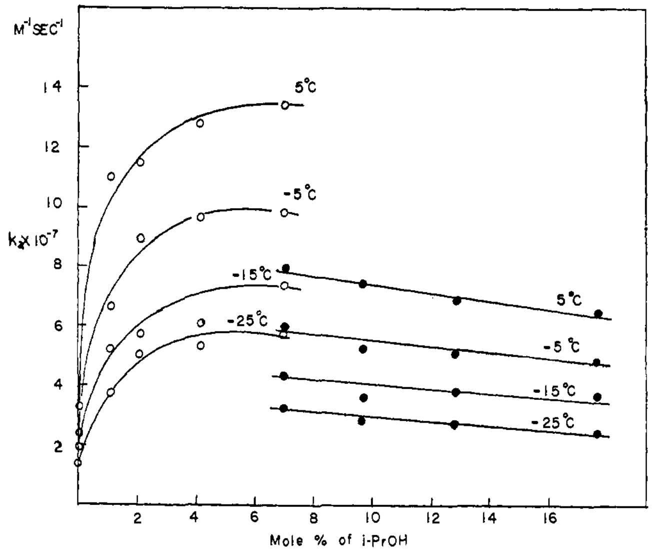


Figure 8. Changes of apparent rate constants for cation-transfer reactions upon addition of *i*-PrOH at various temperatures: (—○—), measured at $[NaBPh_4] = 7 \times 10^{-3}$ *M*; (—●—), measured at $[NaBPh_4] = 2 \times 10^{-2}$ *M*.

The solvent effects in ketyls are remarkably different from those found in hydrocarbon anions. In hydrocarbon anions the electron-transfer rate is primarily determined by the ion-pair structure. In the presence of a strongly solvating solvent the contact ion pair is converted into a solvent-separated ion pair. The rate for the electron-transfer reaction increases drastically. On the other hand, ketyls remain as contact ion pairs in the presence of strongly solvating solvents, but the rate of electron transfer is affected by the solvation structure.

B. Cation-Transfer Reactions. In the present study it is established that Na^+ is the reacting species in the cation-transfer reaction. The possible reaction intermediate is the triple ion $>\dot{C}O^-(Na^+)_2$ and the reaction course is given by

$$Fl^-Na^+ + Na'^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fl^- \begin{matrix} Na^+ \\ \\ Na'^+ \end{matrix} \underset{k_1}{\overset{k_2}{\rightleftarrows}} Fl^-Na'^+ + Na^+$$

The results of the present study are somewhat different from the results of earlier investigations on the cation-transfer reactions between xanthone ketyl and NaI where the cation-transfer rate was found to be approximately linear with respect to [NaI].[23] This indicates that the cation-transfer reaction takes place between Fl^-Na^+ and Na^+I^-. The rate constant was found to be much faster than for $NaBPh_4$, being $\sim 5 \times 10^8\ M^{-1}$.[6] The possible mechanism in this case is the formation of the quadruplet

$$Fl^-Na^+ + Na'I \underset{k_2}{\overset{k_1}{\rightleftarrows}} Fl^- \begin{matrix} Na^+ \\ \\ Na'^+ \end{matrix} I^- \underset{k_1}{\overset{k_2}{\rightleftarrows}} Fl^-Na'^+ + NaI$$

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[21] F. C. Adam and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 1518 (1958).

[22] P. A. Malachesky, T. A. Miller, T. Layloff, and R. N. Adams, *Proc. Brookhaven Symp., Exch. React.*, 157 (1965). International Atomic Agency, Vienna.

[23] N. Hirota, unpublished results.

The existence of quadruplet ketyl is well known[24] and the existence of the intermediate Fl$^-$(Na$^+$)$_2$I$^-$ seems to be quite reasonable. The slow rate constant in the case of ion pair, Na$^+$BPh$_4^-$, is probably due to the inability of forming quadruplet in this case.

The existences of intermediate triple ion and ion quadruplet in cation-transfer reactions have been confirmed recently in our laboratory in the case of semiquinones.[25]

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Nuclear Magnetic Resonance Studies of Aqueous Urea Solutions

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Contribution from the Unilever Research Laboratory Colworth/Welwyn, The Frythe, Welwyn, Herts, England. *Received October 26, 1971*

Abstract: There has been some controversy about the nature of urea solutions, which are important because of their well-known (but as yet unexplained) effects on the conformational properties of a wide range of water-soluble polymers. There are two theories which fit the thermodynamic data: one postulates that urea associates in solution to form a range of aggregates, while the other suggests that urea induces a shift in the equilibrium between the ordered "bulky" and nonordered "dense" species postulated to exist in water, favoring the dense species for statistical reasons (the model excludes specific urea–urea or urea–water interactions). The present work reports nmr relaxation and chemical shift measurements designed to reveal the nature of the species and interactions present in urea solutions. The data show that the long-range order which is characteristic of pure water is destroyed. Correlation times for tumbling of urea molecules show that there is no urea self-association in solution. Urea–water hydrogen-bonded interactions exist, but are only very short-lived, and do not give rise to any extensive ordered arrangement of urea and water molecules. These results rule out the urea association model and are consistent with urea inducing a change in the water equilibrium without taking part in any specific interactions. Such a change would be expected to influence the conformation of water-soluble polymers (*e.g.*, proteins) by changing the nature of polymer–water interactions.

Although aqueous solutions of nonelectrolytes have not, in general, received the same attention as ionic solutions, much effort has been devoted to gaining an understanding of the molecular interactions responsible for the observed properties of urea–water mixtures. It has been recognized for some time that in its aqueous solutions urea possesses some remarkable properties, *e.g.*, it enhances the solubility of hydrocarbons,[1] inhibits micellar aggregation of surfactants,[2] and affects the conformational properties of a wide range of water-soluble polymers; in particular, there is a large and still rapidly expanding literature on the subject of protein denaturation by urea.[3] Most of the published data on aqueous urea solutions describe their thermodynamic properties. This work has been reviewed and supplemented by Stokes,[4] and more recent determinations of heats and heat capacities of solution[5,6] have filled in some of the few remaining gaps.

The thermodynamic properties of aqueous urea solutions provide a framework into which any interpretation of the properties on the molecular level must fit. Urea is characterized by its surprisingly high solubility (>20 *M* at 25°)[7] and by the almost ideal solutions it forms with water.[4,7] This observation, coupled with the similarity of the limiting heat of solution and the heat of fusion of urea, indicates that urea–water interactions in solution are energetically similar to those of urea–urea in the fused state and to water–water interactions in pure water. The heat capacity of solution[5] is only 6 ± 3 cal mol^{-1} deg^{-1} (*cf.* values of 66 and 50 cal mol^{-1} deg^{-1} for ethane and ethanol, respectively), showing that urea does not promote a temperature-sensitive structure in solution. Further indication of the lack of solvent structuring is provided by the only slight increase in apparent molal volume ϕ_v with concentration and the lack of indication of a sharp minimum, such as is characteristic of monofunctional solutes.[8] Urea solutions also show behavior opposite to that of solutions of alcohols, ethers, amines, and ketones in that the temperature derivative $\partial \ln \phi_v/\partial T$ is large and positive, becoming smaller at higher temperatures.

Two different formalisms have been employed to account for the observed physical properties of urea–water mixtures.[9] Stokes has adopted the model of urea association, first considered by Schellman[12a] and

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