

chloride) syringed in. Then the fluoroalkyl iodide was syringed into the cell (usually *ca.* 4 μ l, 0.0056 g, 2.5×10^{-5} mole). In the case of gases the substrate was distilled under vacuum into the cell by means of a small vacuum manifold. The solution was shaken vigorously and freeze degassed at least twice, warmed, photolyzed, and analyzed by esr.^{35,36}

(35) Freshly prepared solutions of NOMP had to be used for each sample, and remained diamagnetic if kept carefully covered from light.

Acknowledgment. The author is indebted to Dr. Donald J. Burton for helpful discussions, and to Phillips Petroleum Co. for financial aid.

However, "aged" NOMP solutions became paramagnetic due to photolysis by visible light to form *t*-butyl radicals. NOMP is monomeric in solution and susceptible to photolysis, while it is a stable dimer in the solid state.¹

(36) No esr signals were observed if the samples were not photolyzed.

Properties of Ion Pairs in Solution. The Reaction of Pyridinium Iodide Charge-Transfer Complexes with Methyl *p*-Toluenesulfonate

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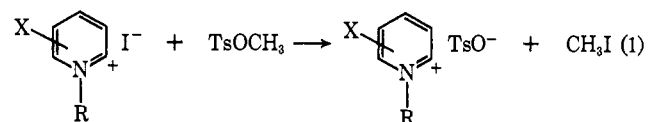
Abstract: This paper presents a general survey of the relationships between some macroscopic and microscopic properties of pyridinium iodide salts in a variety of solvents. The properties investigated are transition energy (E_t), solubility (S), ion-pair dissociation constant (K_d), and rate constant for the nucleophilic displacement reaction of pyridinium iodide ion pairs (k_p) and free iodide ions (k_i) with methyl tosylate. In the absence of specific solvent-solute interactions, ion pair and neutral polar species are shown to exhibit similar solvation properties. The E_t values may be related to the kinetic and bulk thermodynamic parameters. Deviations which occur are related to specific interactions. The pyridinium iodide system is demonstrated to be of potentially great utility in the study of the solution properties of nonspherical cation-spherical anion ion pairs, the charge-transfer contribution to the ground state being small except at low E_t values.

A number of studies have been directed toward an examination of the effect of ion pairing on nucleophilic reactions, such as nucleophilic displacements by halide ions¹⁻³ and the alkylation of oxime salts.⁴ A major difficulty in studies of this type is the lack of a method of directly following the ion pair concentration, since the ion pairs do not usually possess a readily measurable property (*e.g.*, a characteristic absorption band). The usual method employed in these kinetic studies is some form of titration which yields the total nucleophile concentration (*i.e.*, free ion plus ion pair). Conductance measurements may be used to obtain ion pair dissociation constants (K_d) which can then be applied to the kinetic data to obtain the rate constants k_f (for the free ion) and k_p (for the ion pair). However, care must be taken that any relationships obtained in this manner are not significantly sensitive to the value chosen for the distance parameter in the calculation of K_d .³ A further consideration is that during a given kinetic run, the degree of dissociation (α) of the ion pair changes (except for isotopic exchange reactions). Therefore, in obtaining the apparent rate constant (k), initial rates (which are often difficult to obtain) should be used. The rate constant may be obtained by following the reaction over a period of time providing that the extent of reaction is large enough to give a

sufficiently accurate value of k but small enough so that α does not change appreciably.^{2,3}

The pyridinium iodide ion pair has a characteristic charge transfer (c-t) absorption band in the visible or near uv, the frequency depending upon the substituent(s). The position of this c-t band for 4-carbomethoxy-1-ethylpyridinium iodide is the basis of Z values, an empirical measure of solvent polarity.⁵ Thus, the concentration of the ion pair may be followed spectrophotometrically during the course of a reaction.

We have therefore decided to examine a nucleophilic displacement reaction involving pyridinium iodide. Methyl tosylate (TsOCH_3) undergoes an anion exchange reaction with 1-alkylpyridinium iodides in various solvents as shown in eq 1.^{6,7} In the present paper we report the results of studies on this system.



Results

The salt used for the kinetic, dissociation, and solubility studies is 1-ethyl-4-cyanopyridinium iodide. This choice was based on its fairly good solubility in

(1) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, 24 (1960).

(2) W. M. Weaver and J. D. Hutchison, *J. Amer. Chem. Soc.*, 86, 261 (1964).

(3) N. N. Lichtin, M. S. Puar, and B. Wasserman, *ibid.*, 89, 6677 (1967).

(4) S. G. Smith and D. V. Milligan, *ibid.*, 90, 2393 (1968).

(5) E. M. Kosower, *ibid.*, 80, 3253 (1958).

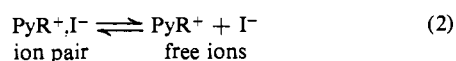
(6) E. J. Poziomek, unpublished results.

(7) This type of anion exchange reaction with 1-alkylpyridinium iodides has been used for synthetic purposes. For example, see B. E. Hackley, Jr., E. J. Poziomek, G. M. Steinberg, and W. A. Mosher, *J. Org. Chem.*, 27, 4220 (1962).

many solvents, its low transition energy (E_t), and its ease of preparation and purification. Additionally, there is a good linear correlation between Z values and E_t .⁵ A number of other pyridinium iodides were also studied, but only in one solvent (CH_2Cl_2). This was done in order to investigate the effect of structure and transition energy on reaction rate.

Dissociation Constants. The possible species present in a salt solution may be grouped into three general categories: contact or intimate ion pairs, solvent-separated (by one or more solvent molecules) ion pairs, and free (solvated) ions. Although the visible c-t band should arise only from the contact ion pairs,^{5,8} a spectrophotometric determination of the dissociation constant for a pyridinium iodide salt will count solvent-separated ion pairs (if any are present) as ion pairs and not as free ions.

Our calculations are based on the equilibrium given in eq 2. If in a given solvent the absorbance *vs.* con-



centration curve follows Beer's law, then the salt will be treated as though it were completely associated in that solvent ($K_d = 0$). By this it is meant that any dissociation which may occur is below the limit of detection of our experimental method.⁹

The dissociation constants calculated from the spectrophotometric measurements are not the true thermodynamic constants. However, they are measured over the same concentration range employed for the kinetic studies ($5 \times 10^{-4} - 1 \times 10^{-2} M$) and will be employed for the kinetic computations.

The values of K_d are determined by use of the equation given by Keefer and Andrews¹⁰ and Ross.¹¹ The equation for the equilibrium of interest here (2) is given by

$$\frac{X}{D} = \frac{WK_d}{\epsilon} + \frac{1}{\epsilon} \quad (3)$$

where $X = c_0^2/(2c_0 - z)$, $W = 1/(2c_0 - z)$, c_0 is the initial pyridinium iodide concentration, z is the concentration of the complex (ion pair), ϵ is the extinction coefficient, K_d is the dissociation constant, and D is the optical density. This method has been used by Kosower and Burbach¹² for the determination of the equilibrium constants of some pyridinium iodides in water.

The calculations were performed by computer using an iterative procedure. An initial choice of z was used to calculate K_d (by the method of least squares). From this value of K_d , a value of z was calculated and the procedure repeated until constant values of K_d and ϵ

(8) It is difficult to see how a solvent-separated ion pair could have a c-t band in the visible, while the free iodide ion c-t band (from I^- to the solvent "cage," or in some cases perhaps to a specific solvent molecule) is in the far uv (60–80 kcal/mol as compared with 125–140 kcal/mol). In any event, the c-t transition energies would be in the order $\text{I}^- >$ solvent separated ion pair $>$ contact ion pair. Since the visible c-t band is the lowest frequency band observed, it is reasonable to assign it to the contact ion pair.

(9) Using cells with a path length of 1 cm and initial salt concentrations in the range $5 \times 10^{-4} - 1 \times 10^{-2} M$, this limit corresponds to $K_d = 1 \times 10^{-4} M$.

(10) R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **74**, 1891 (1952).

(11) S. D. Ross, M. Bassin, M. Finkelstein, and W. A. Leach, *ibid.*, **76**, 69 (1954), and subsequent papers.

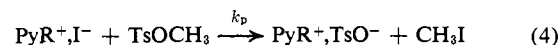
(12) E. M. Kosower and J. C. Burbach, *ibid.*, **78** (1956).

were obtained (usually, about ten iterations were required). The final values of K_d and ϵ did not depend upon the initial choice of z ($0 \leq z \leq c_0$). The values of K_d and ϵ obtained for 4-cyano-1-methylpyridinium iodide in various solvents are given in Table I.¹³

Table I. Dissociation Constants for 4-Cyano-1-ethylpyridinium Iodide in Various Solvents

Solvent	E_t , kcal mol ⁻¹	$10^3 K_d$, M	ϵ , l. mol ⁻¹ cm ⁻¹	T , °C
CHCl_3	57.8	0	1040	25
CH_2Cl_2	59.3	0	1200	27
Acetone	62.2	2.64	816	27
DMF	65.3	39.6	422	26
Methyl formate	66.6	0	810	26
<i>t</i> -AmOH	66.6	0	1033	25
CH_3CN	68.1	10.4	330	25
<i>i</i> -PrOH	72.4	0.31	748	25
EtOH	75.8	2.13	429	27

Kinetics. In all cases, the tosylate concentration was sufficiently larger than the pyridinium iodide concentration so that it effectively did not vary over the course of the reaction. In solvents of low dielectric constant ($K_d < 0.1$), the data will be treated by use of the reaction mechanism given by eq 4. The rate law



will then be given by eq 5, and is pseudo first order in the pyridinium iodide concentration. Then k_{obsd} is

$$\frac{d(\text{PyR}^+\text{I}^-)}{dt} = -k_p(\text{TsOCH}_3)(\text{PyR}^+\text{I}^-) = -k_{\text{obsd}}(\text{PyR}^+\text{I}^-) \quad (5)$$

obtained from a plot of $\ln D$ (D is the optical density) *vs.* time (t) and the bimolecular rate constant by dividing k_{obsd} by the tosylate concentration. Plots of $\ln D$ *vs.* t gave good straight lines within experimental error.

As will be seen below, if there are free ions present which are also reacting then the observed second-order rate constant will depend upon the initial pyridinium iodide concentration. To ensure that the kinetics obeyed a true second-order rate law, the initial pyridinium iodide concentration was varied from $5 \times 10^{-4} - 1.5 \times 10^{-3} M$ in CH_2Cl_2 . The rate constants obtained were the same within experimental error ($\pm 4\%$ for this case). The rate constant did exhibit a dependence on the tosylate concentration (see data in Table II). However, at low tosylate concentrations the second order rate constant does not change, the values for tosylate concentrations of 0.05 and 0.10 M being the same. The variation of rate constants with tosylate concentration is ascribed to a solvent effect. If TsOCH_3 is more polar than CH_2Cl_2 , the rate constant would be expected to increase with increasing concentration. The increase of E_t (Table II) with in-

(13) As pointed out by one of the referees, since contact and solvent-separated ion pairs will be counted together, the derived extinction coefficient will be lowered if solvent-separated ion pairs are in fact present. Of course, a change in solvent could itself produce a change in ϵ , but it is possible that some of the very low ϵ values in Table I indicate the presence of solvent-separated ion pairs.

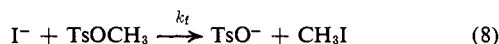
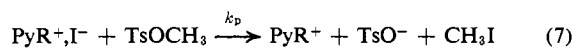
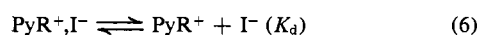
creasing TsOCH₃ concentration is consistent with this view. The pyridinium iodide is thus partially solvated by TsOCH₃, and this in turn affects the rate when the tosylate concentration becomes sufficiently high.

Table II. Observed Rate Constants for the Reaction of 4-Cyano-1-ethylpyridinium Iodide in Various Solvents

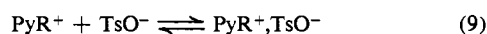
TsOCH ₃ , <i>M</i>	10 ³ <i>k</i> , l. mol ⁻¹ min ⁻¹	<i>T</i> , °C	<i>E</i> _t , kcal/mol
CHCl ₃ (PyI) ₀ ^a = 1.00 × 10 ⁻³ <i>M</i>			
0.30	3.4 ± 0.1	25.5	62.5
0.50	3.6 ± 0.1	25.5	63.4
CH ₂ Cl ₂ (PyI) ₀ = 1.00 × 10 ⁻³ <i>M</i>			
0.05	6.0 ± 0.1	27	59.4
0.10	6.0 ± 0.1	27	59.9
0.20	6.9 ± 0.1	27	60.0
0.30	8.1 ± 0.1	27	60.2
0.40	8.8 ± 0.1	27	60.4
0.50	9.3 ± 0.1	27	60.6
0.60	10.3 ± 0.1	27	61.0
0.70	11.6 ± 0.1	27	61.2
0.10	3.2 ± 0.1	20	60.2
0.10	0.5 ± 0.1	0	
Acetone (PyI) ₀ = 2.50 × 10 ⁻³ <i>M</i>			
0.02	140 ± 2	27	61.9
0.04	143 ± 2	27	61.6
0.08	143 ± 2	27	61.3
0.12	142 ± 2	27	61.0
0.20	133 ± 2	27	60.4
DMF (PyI) ₀ = 0.01 <i>M</i>			
0.10	130 ± 20	26	65.0
Methyl formate (PyI) ₀ = 2.00 × 10 ⁻³			
0.20	16 ± 1	26	67.2
0.40	19 ± 1	26	67.5
0.60	22 ± 1	26	
<i>t</i> -AmOH (PyI) ₀ = 1.00 × 10 ⁻³ <i>M</i>			
0.10	21 ± 2	24.5	67.0
0.10	1.7 ± 0.3	0	
CH ₃ CN (PyI) ₀ = 8.25 × 10 ⁻³ <i>M</i>			
0.13	12 ± 2	25	68.0
<i>i</i> -PrOH (PyI) ₀ = 2.00 × 10 ⁻³ <i>M</i>			
0.10	23 ± 9	25	72.4

^a Initial pyridinium iodide concentration.

In solvents of higher dielectric constant (*K*_d > 0.1) the analysis of the kinetic data is based on the following scheme



Since pyridinium tosylate is undoubtedly dissociated to a greater extent than pyridinium iodide, the association of pyridinium and tosylate ions (eq 9) has been ignored.



This may become less valid near the end of the reaction and the calculations are therefore based on data up to about 50–60% reaction.¹⁴

The rate expression for the above scheme (eq 6–8) can be integrated exactly, leading to an equation which appears rather complicated (eq 10)

(14) The pyridinium iodide–tosylate reaction goes to completion.

$$\ln c + \left(\frac{1}{1 + K_0} \right) \frac{k_p}{k_t} \ln \left[\frac{c_0 + (k_t/k_p) K_d - c}{c_0 - c} \right] + \left(\frac{K_0}{1 + K_0} \right) \ln \left[\frac{(c_0 + (k_t/k_p) K_d - c)^{k_t/k_p}}{c_0 - c} \right] = - \left(\frac{k_p + k_t K_0}{1 + K_0} \right) t + (\text{integration constant}) \quad (10)$$

where *c* = pyridinium iodide ion pair concentration, *c*₀ = initial salt concentration, and *K*₀ = *K*_d/*c*₀. The other symbols are as previously defined. However, a plot of ln *D* vs. *t* for these systems yields a straight line within experimental error, indicating that the second and third terms on the left-hand side of eq 10 are either small or self cancelling and may be ignored. Thus, the apparent second-order rate constant (*k*) is given by eq 11, and will vary with *c*₀

$$k = \frac{k_p + k_t K_0}{1 + K_0} \quad (11)$$

Rearranging eq 11, we obtain

$$k = (k_p - k_t) \left(\frac{1}{1 + K_0} \right) + k_t \quad (12)$$

and a plot of *k* vs. (1 + *K*₀)⁻¹ should yield a straight line with slope *k*_p - *k*_t and intercept *k*_t. This plot is shown in Figure 1. The data for acetone and acetonitrile are given in Table III.

Table III. Kinetic Parameters for the Reaction of 4-Cyano-1-ethylpyridinium Iodide in Acetone and Acetonitrile

(PyI) ₀ ^b	Acetone ^a		
	<i>k</i> ^c	<i>k</i> ₀ ^d	(1 + <i>K</i> ₀) ⁻¹
1.02	1.39 ± 0.02	2.59	0.278
2.04	1.11 ± 0.02	1.29	0.436
3.06	1.10 ± 0.02	0.864	0.536
4.08	1.05 ± 0.02	0.648	0.608
(PyI) ₀ ^e	CH ₃ CN ^f		
	<i>k</i> ^g	<i>K</i> ₀ ^d	(1 × <i>K</i> ₀ ^d) ⁻¹
0.40	1.54 ± 0.09	2.60	0.278
0.70	1.47 ± 0.07	1.49	0.402
1.00	1.45 ± 0.05	1.04	0.490
2.00	1.29 ± 0.05	0.52	0.658

^a (TsOCH₃) = 0.04 *M*; temp = 24°. ^b Initial pyridinium iodide concentration, *M* × 10³. ^c Observed second-order rate constant, l. mol⁻¹ min⁻¹. ^d *K*₀ = *K*_d/(PyI)₀. Values of *K*_d from Table I. ^e Initial pyridinium iodide concentration, *M* × 10³. ^f Observed second-order rate constant, l. mol⁻¹ min⁻¹ × 10. ^g (TsOCH₃) = 0.02 *M*; temp = 24°.

As discussed for CH₂Cl₂, the rate constant does not vary with tosylate concentration when it is below about 0.1 *M*, and in every case the rate constant increases or decreases in the same direction as *E*_t (Table II). This supports the contention that at sufficiently high tosylate concentrations the solvent no longer functions as a "pure" solvent.

The rate data for fixed initial salt concentrations of 4-cyano-1-ethylpyridinium iodide are given in Table II. The data for a number of different pyridinium iodides in CH₂Cl₂ are given in Table IV. The values of *k*_p and *k*_t for the 4-cyano salt (for those solvents in which they were obtained) are collected in Table V. In order to eliminate the substrate–solvent effect, the values in Table V are for TsOCH₃ concentrations of

0.1 *M* or less. In those cases for which the measurements are all above this concentration, the numbers were obtained by extrapolation to 0.1 *M* (CHCl_3 and methyl formate).

Solubilities. The solubility (*s*) of 4-cyano-1-ethylpyridinium iodide in various solvents was measured for the purpose of examining correlations with E_t values and dissociation constants. These data are given in Table VI.

Table IV. Rate Constants of Some Substituted 1-Alkylpyridinium Iodides in Methylene Chloride^a

Substituent ^b	1-Alkyl	E_t	10^2k (± 0.1)	T , $^\circ\text{C}$	10^2k (25°) ^c
4-CN	C_2H_5	59.3	6.0	27	4.9
3-CN	C_2H_5	66.1	6.2	26	5.5
2-CN	C_2H_5	61.1	8.1	26	7.1
2-COOEt	C_2H_5	68.5	14.0	29.5	8.8
4-A	CH_3	61.1	5.3	23	6.6
4-B	CH_3	69.5	6.0	23	7.5
4-C	CH_3	62.0	5.1	22	6.9
4-C	CH_3	62.0	10.6	30	6.9
4-C	CH_3	62.0	0.4	0	6.9

^a Initial pyridinium iodide concentration = 1.00×10^{-3} *M*; tosylate concentration = 0.10 *M*; k in $\text{l. mol}^{-1} \text{min}^{-1}$; E_t in kcal mol^{-1} . ^b A, $-\text{C}(-\text{CN})=\text{N}-\text{OCH}_2\text{C}_6\text{H}_5$; B, $-\text{CH}=\text{NO}-(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$; C, $-\text{C}(-\text{CN})=\text{NO}(\text{CH}_2)_2\text{CH}_3$. ^c Corrected to 25° using an activation energy of 17 kcal mol^{-1} .

Table V. Ion Pair and Free Ion Rate Constants for 4-Cyano-1-ethylpyridinium Iodide in Various Solvents

Solvent	$10^2k_p^a$	$10^2k_f^a$	T , $^\circ\text{C}$	10^2k_p (25°) ^b
CH_2Cl_2	6.0 ± 0.1		27	4.9
CHCl_3	3.2 ± 0.3		25.5	3.0
Me formate	14.5 ± 1.5^c		26	13
<i>t</i> -AmOH	21 ± 2		24.5	22
Acetone	64 ± 23	162 ± 12	24	70
CH_3CN	10.8 ± 1.8	17.5 ± 1.5	24	12

^a Ion pair (k_p) and free ion (k_f) rate constants in $\text{l. mol}^{-1} \text{min}^{-1}$. ^b Corrected to 25° using an activation energy of 17 kcal mol^{-1} . ^c Extrapolated to a tosylate concentration of 0.10 *M*.

Table VI. Solubility Data for 4-Cyano-1-ethylpyridinium Iodide in Various Solvents at 25°

Solvent	$10^2\bar{V}^a$	10^3S^b	$10^4\bar{V}S$
CH_2Cl_2	6.36	11.0	7.00
CHCl_3	7.99	2.9	2.32
Me formate	6.13	229	140
Acetone	7.33	107	78.4
CH_3CN	5.25	795	417
<i>t</i> -AmOH	10.9	2.8	3.05
<i>i</i> -PrOH	7.66	11.2	8.59
EtOH	5.84	103	60.1

^a Molar volume of pure solvent in l. mol^{-1} . ^b Solubility in mol l^{-1} .

The solubility in DMF is too great to be measured. However, a plot of dissociation constant *vs.* solubility gives a reasonably linear correlation. If this correlation also holds for DMF, the solubility would be on the order of 3 *M*.

Discussion

The behavior of a solute in a solvent is dependent upon the nature of the various solvent and solute

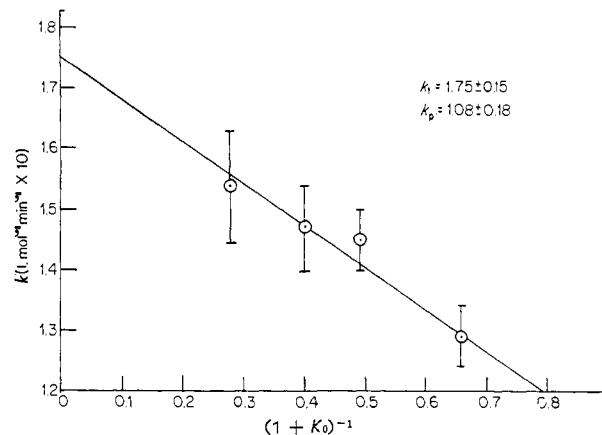


Figure 1. Dependence of observed second-order rate constant on initial salt concentration for reaction of 4-cyano-1-ethylpyridinium iodide with methyl tosylate in acetonitrile; k = rate constant, $K_0 = K_4c_0$, where c_0 is the initial pyridinium iodide concentration.

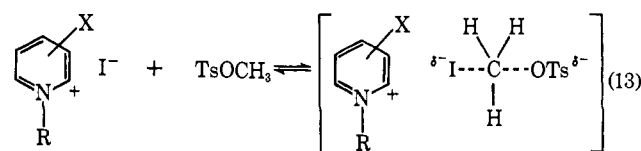
interactions. These interactions may be nonspecific (direct) such as van der Waals, dipole-dipole, etc., or specific such as hydrogen bonding, complex formation, steric hindrance of free rotation, etc.

The properties which determine the direct interactions, for example dipole moments, are characteristic of the given substance. Thus, to a first approximation, the dipole moment of a given solvent-solute is the same regardless of the solute or solvent, respectively. The specific interactions depend on the system itself. For example, a solute which hydrogen bonds with one solvent may not do so with another, and *vice versa*.

Therefore, for a given solute in a series of different solvents, a correlation between the macroscopic and microscopic properties of the solute (*e.g.*, solute activity coefficient γ and *c-t* transition energy E_t , respectively) will be obtained only if specific interactions are either absent or constant throughout the series.

The difference in E_t values for a given pyridinium iodide salt in two different solvents has been related to the free energy of transfer of the ion pair dipole.⁵ It would then be expected that a plot of $\log \gamma$ *vs.* E_t for a given solute in a group of different solvents would give a straight line providing that specific interactions are either absent or constant. Deviation of a particular solvent from this straight line may then be ascribed to the presence (or absence) of a specific interaction which the rest of the group does or does not possess. Similarly, two groups of solvents may exhibit separate straight-line behavior, the separation again being due to a specific interaction possessed by the members of one group and not the other. The results of this study will be discussed in terms of the above considerations.

Ion Pair Reaction. The reaction of the pyridinium iodide ion pair with methyl tosylate to form the transition state¹⁵ is shown in eq 13. Both the pyridinium



(15) The orientation of the pyridinium ion in both the reactant- and transition-state ion pairs is not known and should not be inferred from eq 13.

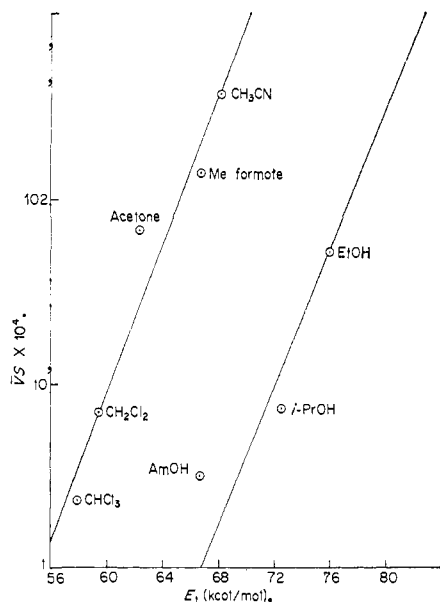


Figure 2. Solubility vs. CT transition energy for 4-cyano-1-ethylpyridinium iodide in various solvents.

iodide and the transition state are ion pairs which differ only in the nature of the anion.

The reactant and transition-state ion pairs should exhibit similar solvation properties. This is consistent with the linear relations obtained between Z values, E_t values for other pyridinium iodides and N -oxides, and $E_t(30)$ values.¹⁶

Thus, although the reactant- and transition-state ion pairs should exhibit much larger solvent effects¹⁷ than the substrate, these should largely cancel. The overall effect of solvent on the rate constant (k_p) will then be small.

The values of k_p (Table V) bear out this expectation. All of the rate constants (except for acetone and possibly DMF) fall in the range $(12 \pm 10) \times 10^{-2}$ l. mol⁻¹ min⁻¹. The variation in k_p from the lowest (CHCl_3) to the highest (acetone) is only by a factor of 20. An examination of the values of k_p in different solvents therefore yields little information concerning the solvation properties of either the reactant or transition-state ion pairs. The reactant ion pair, however, may be studied separately, and combined with the k_p data may then yield information concerning the transition state. The ratio of rate constants for the same reaction (eq 13) in two different solvents is given by eq 14,¹⁸ where γ_i is the activity coefficient in solvent

$$\log \frac{k_1}{k_2} = \log \left(\frac{\gamma_1}{\gamma_2} \right)_{\text{Py}^+\text{I}^-} + \log \left(\frac{\gamma_1}{\gamma_2} \right)_{\text{TSOCH}_3} - \log \left(\frac{\gamma_1}{\gamma_2} \right)_{\pm} \quad (14)$$

i relative to a common standard state and \pm represents the transition state.¹⁹

(16) E. M. Kosower, "Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, pp 293-305.

(17) The magnitude of the solvent effect is the change in free energy of solution with change in solvent.

(18) (a) N. Bjerrum, *Z. Physik. Chem.*, **108**, 82 (1924); (b) J. N. Brønsted, *ibid.*, **102**, 169 (1922).

(19) Since the values of k_p were independent of salt concentration over the range of relatively low concentrations studied, the variation of k_p (and γ) with concentration has been ignored. The γ_i values therefore

If to a first approximation we may ignore the substrate term in eq 14, then we may write

$$\log \left(\frac{\gamma_1}{\gamma_2} \right)_{\pm} \approx \log \left(\frac{\gamma_1}{\gamma_2} \right)_{\text{Py}^+\text{I}^-} - \log \frac{k_1}{k_2} \quad (15)$$

The solvation properties (γ_i) of the pyridinium iodide ion pair will be examined next. From these and the k_p data, the γ_i for the transition state will be obtained by use of eq 15.

Reactant Ion Pair. The variation of $\log \gamma$ of the 4-cyano-1-ethylpyridinium iodide ion pair with solvent E_t is shown in Figure 2. The E_t are essentially Z values,⁵ and the solubilities are related to the activity coefficients.²⁰ The relationship is only approximate since we have ignored the variation of γ with concentration. This will not obscure the qualitative features we wish to discuss. The Z values have been related to the free energy of formation of the cybotactic region⁵ (which presumably consists of the first few solvent shells about the solute). If this constitutes the entire free energy of solution (or is proportional to it) then a plot of $\ln \gamma$ (or $\ln \bar{V}S$) for the ion pair would be expected to yield a single linear correlation as previously mentioned. An examination of Figure 2 shows that the alcohols form a separate group. This seems reasonable since for structured solvents a disturbance in the cybotactic region may be strongly propagated into the bulk. It should be noted that acetone deviates a bit more than the others in the nonhydroxylic group, and that DMF (whose E_t value is between acetone and methyl formate) would be completely off the scale. A possible explanation may be the suggestion that solvents such as DMF, acetone, and CH_3CN form weak complexes with iodide.²¹

If the above is the case, then the effect of this complexation on the solubility is in the order $\text{DMF} \gg \text{acetone} > \text{CH}_3\text{CN}$. It is clear that the "local" properties of the solvent (in the vicinity of the solute) are related to the bulk thermodynamic properties, but that long-range structural and specific interaction effects are important to the latter. Therefore, local properties (e.g., E_t) will correlate with bulk thermodynamic properties (e.g., activity coefficient) only when the interaction and structural effects are either negligible or constant.

Transition-State Ion Pair. Having obtained the values of γ for the reactant ion pair, we now consider the solvation properties of the transition state ion pair. From the relationship between γ and $\bar{V}S$ ²⁰ and eq 15, we obtain eq 16.

$$\log \frac{(k_p \bar{V}S)_1}{(k_p \bar{V}S)_2} \approx -\log \left(\frac{\gamma_1}{\gamma_2} \right)_{\pm} \quad (16)$$

A plot of $\log k_p \bar{V}S$ vs. E_t is shown in Figure 3. Acetone now shows a considerable positive deviation from the normal "line", while t -AmOH exhibits a negative deviation (as in Figure 2). The slopes of the lines in Figures 4 and 5 are similar, 0.20 and 0.25 kcal⁻¹ mol on a log basis, respectively. We may conclude

represent activity coefficients for transfer of solute from a common reference solvent (standard state) to solvent i .

(20) For our purposes, we have chosen the pure solid as the standard state for both solid and solution. The activity coefficient is then given by $\gamma = 1/\bar{V}S$, where $\bar{V}S$ is the solubility expressed as mole fraction.

(21) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3261 (1958); *ibid.*, **80**, 3267 (1958).

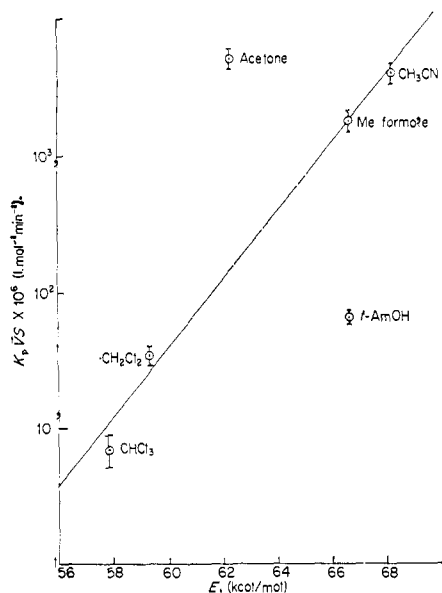


Figure 3. Dependence of transition-state activity coefficient on c-t transition energy for 4-cyano-1-ethylpyridinium iodide in various solvents.

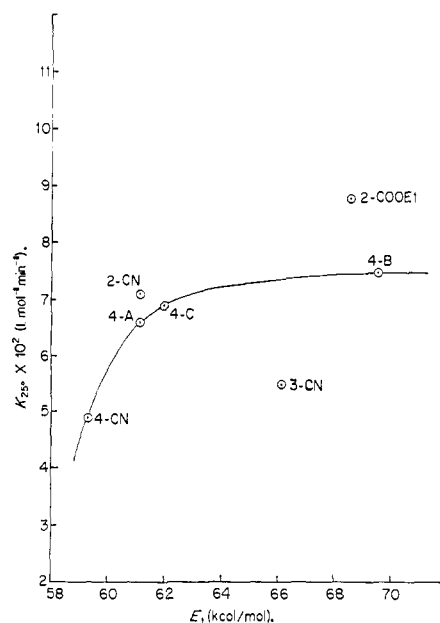


Figure 5. Dependence of ion-pair rate constant for the reaction of some substituted 1-alkylpyridinium iodides and iodide oximes with methyl tosylate in CH_2Cl_2 on CT transition energy (A, $-\text{C}(-\text{CN})=\text{NOCH}_2\text{C}_6\text{H}_5$; B, $-\text{CH}=\text{N}-\text{O}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$; C, $-\text{C}(-\text{CN})=\text{NO}(\text{CH}_2)_2\text{CH}_3$; the 1-alkyl substituent is methyl for 4-A, 4-B, and 4-C, and ethyl for the others).

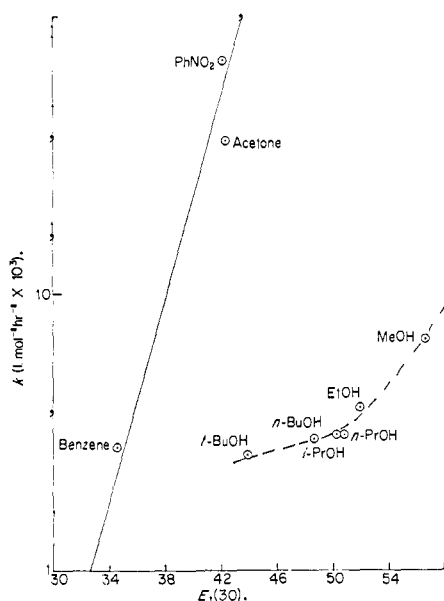


Figure 4. Dependence of rate constant for the reaction ethyl iodide with pyridine on $E_t(30)$ values in various solvents. The rate data are from J. F. Norris and S. N. Prentiss, *J. Amer. Chem. Soc.*, **50**, 3042 (1928).

that the reactant and transition-state ion pairs exhibit similar solvation properties in CH_2Cl_2 , CHCl_3 , CH_3CN , and methyl formate.

The deviation in acetone may arise from the formation of a weak acetone-iodide complex, as previously discussed. If the reactant ion pair carries a complexed molecule of acetone into the transition state, then less solvent reorganization is required and the entropy of activation would be increased. If the complexation is weak, any effect on the enthalpy of activation may be neglected. This implies that if the transition-state ion pair could be isolated and its activity coefficient measured (as was done for the pyridinium iodide salt), then acetone would exhibit no deviation.

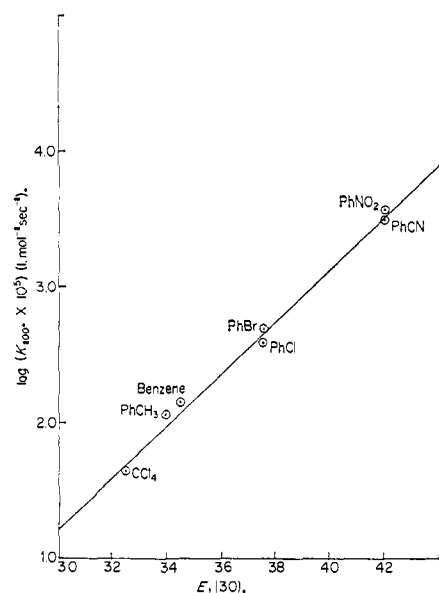
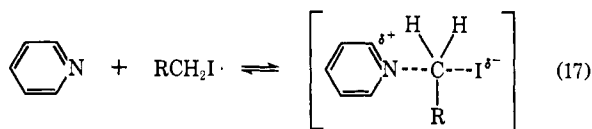


Figure 6. Dependence of rate constant for the reaction of methyl iodide with pyridine on $E_t(30)$ values in various solvents. The rate data are from N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936).

Neutral Polar Transition States. Having examined the reactant- and transition-state ion pair solvation properties, we now wish to examine their applicability to other systems. Since the ion pairs may be considered as highly polar neutral species, it is of interest to compare these results with those for a neutral transition state.

The Menshutkin reaction between two neutral molecules (pyridine and alkyl iodide) leads to the formation of a neutral polar transition state (eq 17)



We will ignore the solvation of the reactants compared with the transition state. In Figure 6 is shown a plot of $\log k$ vs. E_t (30) for CCl_4 and a series of substituted benzenes ($R = \text{H}$), and in Figure 4, for benzene, nitrobenzene, acetone, and a series of alcohols.²²

A good linear correlation is obtained for the solvents in Figure 6. In Figure 4, the linear correlation shown for only three points (benzene, nitrobenzene, and acetone) is based on the behavior of the similar system in Figure 6. Here, as in the pyridinium iodide-methyl tosylate reaction, the rate constants in alcohols are low relative to normal solvents with the same E_t values.

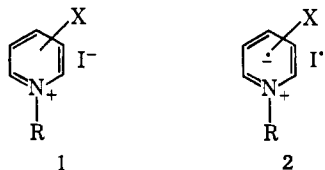
The slopes of the lines in Figures 4 and 6 (with respect to Z values) are 0.26 and 0.24 $\text{kcal}^{-1} \text{mol}$, respectively. On the same basis, the slopes for Figures 2 and 3 are 0.21 and 0.26 $\text{kcal}^{-1} \text{mol}$, respectively. We thus conclude that the neutral polar transition state and the ion pair transition state have similar solvation properties. It may be noted that the normal behavior of acetone for the Menshutkin transition state is consistent with our earlier speculation that thermodynamic and "kinetic" activity coefficients may differ.

Ion Pair Activation Energies. Extensive temperature data were not obtained, and the Arrhenius activation energies were measured only for 4-cyano-1-ethylpyridinium iodide in CH_2Cl_2 and *t*-AmOH, and for O-(*n*-propyl)-4-cyanofornyl-1-methylpyridinium iodide oxime in CH_2Cl_2 . These data are given below.

Salt	Solvent	E_a , kcal/mol
	CH_2Cl_2	16.3 ± 1
	<i>t</i> -AmOH	17.4 ± 2
	CH_2Cl_2	17.8 ± 1

The activation energy for the methyl tosylate-iodide ion pair reaction may be taken as about 17 kcal/mol. A more extensive and accurate determination is needed to examine the influence of solvent and ion pair structure on the activation parameters.

Ion Pair Substituent Effects. A pyridinium iodide ion pair differs from a simple electrostatic ion pair (e.g., a tetraalkylammonium halide) in that both the electrostatic (1) and charge-transfer (2) resonance forms may contribute to the ground state.



Although the contribution of 2 would be expected to be small, it may nonetheless exert a measurable influence on the rate constant. It is expected that the relative contribution of 2 would be related to the magnitude of the transition energy, increasing as E_t decreases.

(22) $E_t(30)$ values were used since they are available for all of the solvents. The Z values, $E_t(30)$ values, and other E_t values are linearly related and can be interconverted.

Among the seven salts studied (Table IV), the rate constant varies by less than a factor of two. The effect of the substituents on k_p is, as expected, small but measurable. The variation of k_p with E_t is shown in Figure 5. A smooth curve may be drawn through the points for the four-substituted salts. At high E_t values as the contribution of 2 becomes increasingly less important, k_p levels off. At low E_t values k_p drops sharply and should approach zero as E_t approaches the value for spontaneous electron transfer.

It is clear, however, that not only the E_t value but the position of a given substituent is important. If the charge-transfer resonance form 2 requires close approach of iodide to the pyridinium nitrogen, then steric hindrance by the substituent may affect k_p . This should not be a consideration for the compounds in this study, since an examination of models shows that even the 2-carboethoxy group will not prevent iodide-nitrogen contact.

The substituent may influence the electrostatic interaction 1 by its effect on the dispersal of positive charge. The rate of alkylation of cyanopyridines should be related to the concentration of positive charge on the pyridine nitrogen. Thus, if dispersal of positive charge were the only effect, k_p should be in the order 3-CN > 2-CN, 4-CN²³ (if the iodide ion is located near the pyridinium nitrogen). The actual order (Table IV) is 2-CN > 3-CN > 4-CN. Furthermore, the iodide ion may at least in some cases, be located near the substituent rather than near the pyridinium nitrogen. There may then be some question as to whether E_t will give a true indication of the relative contribution of 2 to the ground state, especially in the case of three-substituted pyridinium salts where the substituent is not conjugated with the pyridinium nitrogen.

All of these factors are interrelated to some extent, and a more exhaustive study will be needed to determine their relative contributions to the ion pair reactivity.

Free Ions. Values for both k_p and k_f were obtained only for CH_3CN and acetone (Table V). These numbers are subject to fairly large uncertainties, and to obtain more accurate values a larger number of concentrations over a wider range should be examined. However, it may be seen that $k_f > k_p$ as would be expected from consideration of the cation-anion electrostatic interaction. This interaction would tend to decrease the reactivity of the paired nucleophilic ion.

The values of k_f for acetone ($E_t = 62.2$) and CH_3CN ($E_t = 68.1$) are 1.6 ± 0.1 and $0.18 \pm 0.01 \text{ l. mol}^{-1} \text{ min}^{-1}$, respectively. This is in accord with the expectation that k_f should decrease as the ability of the solvent to solvate the anion (either by direct or specific solvation or both) increases. Studies of this type for a wide range of solvents should provide information on the effect of both solvent polarity (direct solvation) and specific interactions on both free ions and ion pairs.

Summary. The reactions and solvation properties of ion pairs may be conveniently studied spectrophotometrically by the use of pyridinium iodide c-t complexes. These salts provide an added advantage in that the energy of the c-t band (E_t) is also a microscopic measure of solvent polarity. Additionally, although these ion

(23) E. J. Poziomek, unpublished results.

pairs possess some c-t contribution to the ground state, the effect on k_p will be small except at low E_t values.

When specific interaction effects are either absent or constant, similar species (ground- and transition-state ion pairs and polar neutral species) have similar solvation properties. The slope of the $\log \gamma$ vs. E_t line for these species is 0.24 ± 0.03 kcal mol⁻¹ with respect to Z values. Thus the change in free energy of solvation for transfer of one of the above solute species from one solvent to another is about one-third of the change in Z value. Deviations in acetone are ascribed to the formation of a weak acetone-iodide complex and in *t*-AmOH to hydrogen bonding.

More extensive data are needed before any attempts at constructing detailed models or performing quantitative calculations are made. However, the utility of the pyridinium iodide system for study of the solution properties of nonspherical cation-spherical anion ion pairs has been demonstrated.

Experimental Section

Compounds.²⁴ **4-Cyano-1-ethylpyridinium Iodide.** Ethyl iodide (45 ml), 4-cyanopyridine (28 g), and acetone (120 ml) were stirred in the dark for 3 days. The bright yellow solid which formed was filtered, washed with methylene chloride, and dried in a vacuum desiccator over P₂O₅; mp 139–140° dec.

Anal. Calcd for C₈H₉IN₂: C, 36.9; H, 3.4; I, 48.9; N, 10.8. Found: C, 36.7; H, 3.2; I, 48.8; N, 10.7.

3-Cyano-1-ethylpyridinium Iodide. Ethyl iodide (25 ml), 3-cyanopyridine (12 g), and acetone (30 ml) were stirred in the dark for 1 day. The resulting yellow solid was filtered, washed with acetone, and dried in a vacuum desiccator over P₂O₅; mp 192.5–193.5° dec.

Anal. Calcd for C₈H₉IN₂: C, 36.9; H, 3.4; I, 48.9; N, 10.8. Found: C, 37.1; H, 3.5; I, 49.0; N, 10.6.

2-Cyano-1-ethylpyridinium Iodide. Ethyl iodide (25 ml), 2-cyanopyridine (15 ml), and acetone (30 ml) were stirred in the dark for 2 days. Excess ether was added and the precipitate was filtered,

washed with ether, and dried in a vacuum desiccator over P₂O₅; mp 156–158° dec.

Anal. Calcd for C₈H₉IN₂: C, 36.9; H, 3.4; I, 48.9; N, 10.8. Found: C, 36.9; H, 3.5; I, 48.6; N, 10.9.

2-Carboethoxy-1-ethylpyridinium Iodide. Ethyl picolinate (20 ml), ethyl iodide (15 ml), and acetone (50 ml) were refluxed for 2–3 hr and stirred in the dark for about 4 days. About 100 ml of diethyl ether was added, the mixture was stirred for 30 min, then filtered and washed with ether. Enough acetone was added to dissolve about one-third of the solid. The mixture was filtered and the remaining solid was washed with ether. A rubber dam was used to avoid drawing air through the wet solid during the filtration. The procedure was repeated and the product was dried in a vacuum desiccator over P₂O₅; mp 108.5–109.5° dec.

Anal. Calcd for C₁₀H₁₄INO₂: C, 39.0; H, 4.6; N, 4.7. Found C, 39.0; H, 4.0; N, 4.5.

Pyridinium Iodide Oximes. Samples of O-(3-methyl-1-butyl) 4-formyl-1-methylpyridinium iodide oxime, O-(*n*-propyl) 4-cyanoformyl-1-methylpyridinium iodide oxime, and O-benzyl 4-cyanoformyl-1-methylpyridinium iodide oxime were kindly supplied by Tyson.²⁵

Methyl *p*-Toluenesulfonate. A sample of methyl tosylate was purified by fractional distillation under vacuum.

Spectrophotometric Data. All visible absorption data were obtained on a Cary 14 spectrophotometer using 1-cm cells with the solvent as reference. Temperature control was maintained *via* a constant temperature bath with water circulating through a metal block cell holder. Kinetic studies were performed by mixing the reagents, placing a sample in the spectrophotometer, and scanning optical density as a function of time at a fixed wavelength corresponding to the c-t band maximum. A few runs were carried out at 0° by taking samples at various times and obtaining the absorption readings. These reactions were sufficiently slow so that the time lag between withdrawal of the sample and the absorbance measurements (0.5–1 min) did not cause any significant error. Saturated solutions for the solubility studies were prepared by dissolving the salt with heating and then letting the solution slowly cool (with crystallization of the salt) to 25° (usually overnight). An absorbance reading was obtained on an appropriate dilution of the saturated solution and the concentration was determined from the absorbance vs. concentration curve. The results obtained in this manner were quite reproducible.

Analyses. Elemental analyses were performed by the Analytical Research Department, Chemical Research Laboratory, Edgewood Arsenal.

(24) The absence of trace amounts of triiodide in each compound was confirmed spectrophotometrically in each of the solvents used for this study.

(25) B. C. Tyson, Jr., Ph.D. Dissertation, University of Delaware, June 1969.