Direct Observation of Recombination Barriers of Ion Pairs by Dynamic NMR Spectroscopy

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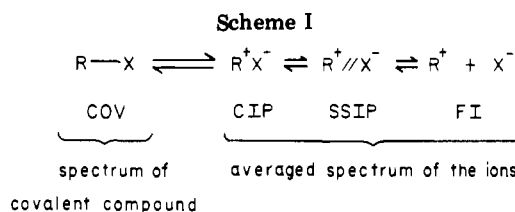
Received March 31, 1981

Ion pairs produced by ionization of covalent organic molecules are often postulated as transient intermediates in mechanistic organic chemistry.[1] That postulate requires at least a small barrier between the energetically elevated ion pair (IP) and the covalent molecule (COV). Before our work, there existed no direct measurement of this barrier.

Rates of recombination of *free ions* (FI) have been measured by means of stopped-flow[2] and pulse-radiolysis[3] methods. In neither technique does the observed rate of ion disappearance normally correspond to the rate of recombination of *ion pairs*. The free energy of the free ions is often much higher than of the ion pair. For instance, the kinetics of recombination of chloride ions and triphenylmethyl cations in 1,2-dichloroethane, which is practically diffusion controlled,[3] allow a barrier of up to about 9 kcal/mol for the ion pair recombination (Figure 1). How high the barrier is depends on the unknown stability of the ion pairs. To construct Figure 1 we have estimated the free energy of the ion pair association as 4–6.4 kcal/mol from the data concerning trityl salts in solvents with similar dielectric constants.[4] The small barrier of 2.5 kcal/mol indicated for recombination of the free ions to form the ion pair follows from the reported overall rate constant $(8 \times 10^{10}$ L/(mol·s).[3] It is apparent that slower recombinations, which occur at rates not controlled by the diffusion of the ions, have rate constants determined by the barrier of the ion pair recombination step to a substantial but seldom specified extent.
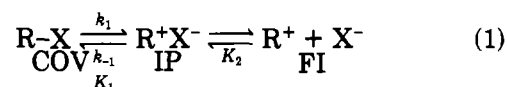
As solvent polarity and/or the stability of the ionic forms is increased, systems are attained in which the free energy difference between ionic and covalent structures is small. In those cases dynamic NMR (DNMR) techniques[5] can be applied in order to determine directly the ion pair recombination barrier provided that the rate is within the NMR time scale.[6] During the last few years, we have studied a number of examples and found remarkably high barriers (up to 16 kcal/mol!)[7] for ion pair recombination.

An advantage of the NMR technique for the study of the equilibrium lies in its capacity to distinguish between covalent molecules and carbocations. At low temperatures the spectrum of the covalent compound

Scheme I

$$R\!-\!X \;\rightleftharpoons\; \overset{+}{R}\overset{-}{X} \;\rightleftharpoons\; \overset{+}{R}/\!/\overset{-}{X} \;\rightleftharpoons\; \overset{+}{R} + \overset{-}{X}$$

$$\underset{\text{COV}}{} \qquad \underset{\text{CIP}}{} \quad \underset{\text{SSIP}}{} \qquad \underset{\text{FI}}{}$$

spectrum of   averaged spectrum of the ions
covalent compound

is usually separated from the spectrum which results from the kinetic averaging of all ionic forms present in the system. In one case we have good evidence that contact ion pairs predominate in the equilibrium of the ionic forms. Furthermore, the ^{1}H and ^{13}C NMR chemical shifts of the covalent form and their relative insensitivities to temperature and solvent variation exclude the possibility of representing such systems as mixtures of covalent molecules and contact ion pairs in rapid equilibrium (see Scheme I). Hence, the observed barriers pertain to the conversion of ion pairs into covalent molecules.

We have never found separate signals for different types of ions, but the occurrence of free ions is indicated if the ratio of the covalent compound to the sum of ions varies with the overall concentration. Hence, we consider in the subsequent discussion solely a reduced Winstein scheme (eq 1) omitting the differentiation

$$\underset{\text{COV}}{R\!-\!X} \underset{\underset{K_1}{k_{-1}}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{IP}}{R^+X^-} \overset{K_2}{\rightleftharpoons} \underset{\text{FI}}{R^+ + X^-} \qquad (1)$$

between contact and solvent-separated ion pairs.

Line-shape analysis of exchange-broadened NMR spectra yields the (pseudo) first order rate constants for

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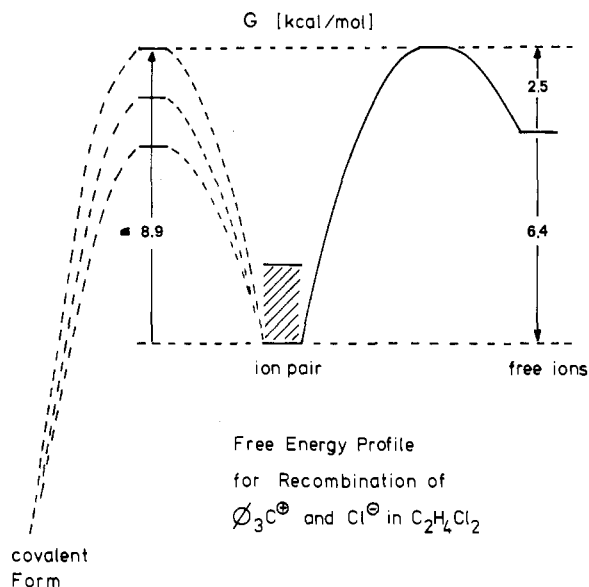
(1) (a) M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions", Vol. 1 and 2, Wiley-Interscience, New York, 1972, 1974; (b) G. A. Olah and P. v. R. Schleyer, Eds., "Carbonium Ions", Vol. 1–4, Interscience Publishers, New York, 1968–1973; (c) T. E. Hogen-Esch, *Adv. Phys. Org. Chem.*, 154 (1977).

(2) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Am. Chem. Soc.*, **89**, 2063 (1967); C. D. Ritchie and P. O. I. Virtanen, *ibid.*, **94**, 4966 (1972); C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972).

(3) L. M. Dorfman, R. J. Sujdak, and B. Bockrath, *Acc. Chem. Res.*, **9**, 352 (1976); L. M. Dorfman and V. M. De Palma, *Pure Appl. Chem.*, **51**, 123 (1979).

(4) Reported free energies of association (298 K) for trityl salts: perchlorate 4.9 kcal/mol in 1,2 dichloroethane[3a] and hexafluoroantimonate 5.3 kcal/mol[3b] and hexachloroantimonate 4.9 kcal/mol,[3c] both in dichloromethane. Higher association is possible with the smaller chloride ion. (a) W. Y. Lee and F. E. Treolar, *J. Phys. Chem.*, **73**, 2458 (1969); (b) W. Gogolczyk, S. Slomkowski, and S. Penczek, *J. Chem. Soc., Perkin Trans. 2*, 1729 (1977); (c) P. M. Bowyer, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. B*, 1511 (1971).

(5) DNMR = dynamic NMR: G. Binsch, H. Kessler, *Angew. Chem.*, **92**, 445 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 411 (1980).

(6) H. Kessler, *Angew. Chem.*, **82**, 237 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

(7) M. Feigel and H. Kessler, *Chem. Ber.*, **111**, 1659 (1978).

G [kcal/mol]

2.5

8.9

6.4

ion pair   free ions

Free Energy Profile

for Recombination of

$\emptyset_3C^\oplus$ and $Cl^\ominus$ in $C_2H_4Cl_2$

covalent
Form

Figure 1. Estimation of the maximal barrier ion pair → covalent form which is in accordance with results of pulse radiolysis measurements.

the transfer of magnetization between individual sites. In the present systems these are the covalent form and the sum of the ions. So we express the rates of disappearance of COV and of the ions with rate constants k_i and k_{-i}, respectively (eq 2). From consideration of

$$-\frac{dc_{COV}}{dt} = k_i c_{COV} - \frac{dc_{ions}}{dt} = k_{-i} c_{ions} \qquad (2)$$

these rate expressions and the actual equilibrium, it follows that

$$k_1 = k_i$$

but

$$k_{-1}c_{IP} = k_{-i}(c_{IP} + c_{FI})$$

or

$$k_{-1} = k_{-i}[1 + (c_{FI}/c_{IP})]$$

If appreciable amounts of free ions are present in the equilibrium, the ion pair recombination k_{-1} is not identical with the "NMR recombination rate" and the ratio of free and paired ions must be specified.

Search for Suitable Systems

Generally, the equilibrium COV ⇌ IP is sensitive to the following four parameters: stability of the cations, stability of the anions, polarity of the solvent, and temperature.

The stability of the cations is represented by the existing pK_{R^+} scale[8] whereas that of the anions is approximated by their basicities, expressed as the pK_a's of the corresponding acids.[9] The media which can be used are aprotic solvents with low melting points, such as SO_2, CD_3CN, CD_2Cl_2, $CDCl_3$, and tetrahydrofuran (THF). Furthermore, one should keep in mind that the equilibrium is shifted strongly toward the ions by lowering the temperature[10] as a result of increased solvation of the ions.

In the beginning, we found suitable systems by trial and error; as examples accumulated, we were able to make the search a bit more systematic by constructing

a three-dimensional plot in which two of the coordinates were pK_{R^+} and pK_a, whereas the third represents the solvent (Figure 2). Each point in the diagram corresponds to a system in which the free energy difference between the covalent form and all ionic forms ($\Delta G^\circ_{COV-ions}$) is approximately zero at temperatures between 200 and 300 K. This experimentally accessible region lies near the shaded surface in Figure 2, which divides it diagonally into two experimentally inaccessible regions. It is evident that all compounds in the upper right-hand region are ionic even in rather unpolar solvents whereas compounds in the lower left hand region are covalent even in liquid SO_2. Typical examples studied, all lying in the shaded surface, involve the rather stable tropylium, cyclopropenylium,[11] and trityl cations.

Triphenylmethyl Chloride

Triphenylmethyl chloride, also known as trityl chloride, is the classical textbook example of an organic molecule able to ionize and dissociate in polar solvents such as liquid SO_2. Although many careful conductivity measurements of Ph_3CCl and its derivatives exist,[12] it is difficult to extract the temperature dependence of the equilibrium constant K_1 (COV ⇌ IP) from these experiments.

In the ^{1}H NMR spectrum of Ph_3CCl in SO_2, separate signals for ions (IP + FI) and COV were observed near the freezing point of the solvent and coalescence occurs around 190–240 K.[13,14] The rather complex exchange of the coupled 5-spin system (Figure 3) was simulated by using an extended version of the DNMR 3 program.[15] The concentration dependence of the trityl chloride equilibrium was investigated in a compound deuterated in all ortho and para positions. Arrhenius plots based on the rates of ionization (k_1) and of overall recombination of the ions (k_{-i}) are shown in Figure 4.

Obviously, since ionization is a first-order process, k_1 is independent of concentration. This rules out strong electrophilic assistance of the ionization by R^+ forming an $R-X^+-R$ species. Such a mechanism would result in higher order kinetics. The rate constant for ion recombination, k_{-1}, must be derived from the experimental pseudo-first-order k_{-i}, with knowledge of the relative amounts of free and paired ions (see above). For that purpose we have used the concentration dependence of the equilibrium K_{ion} determined by the NMR measurements. Combination of the three equations

$$K_{ion} = \frac{c_{FI} + c_{IP}}{c_{COV}} \qquad K_1 = \frac{c_{IP}}{c_{COV}} \qquad K_2 = \frac{\gamma_\pm c_{FI}^2}{c_{IP}}$$

leads to

$$K_{ion} = \left(\frac{K_1 K_2}{\gamma_\pm c_{COV}}\right)^{0.5} + K_1$$

(8) H. H. Freedman in ref 1b, Vol. IV, p 1501.
(9) R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.*, **90**, 319 (1968).
(10) M. Feigel and H. Kessler, *Tetrahedron*, **32**, 1575 (1976).
(11) H. Kessler and A. Friedrich, unpublished results.
(12) N. N. Lichtin, in ref 1b, Vol. 1, p 135; G. Launay and P. Castellonese, *Bull. Soc. Chim. Fr.*, 226 (1978).
(13) M. Feigel and H. Kessler, *Angew. Chem.*, **89**, 266 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 256 (1977).
(14) M. Feigel and H. Kessler, *Chem. Ber.*, **112**, 3715 (1979).
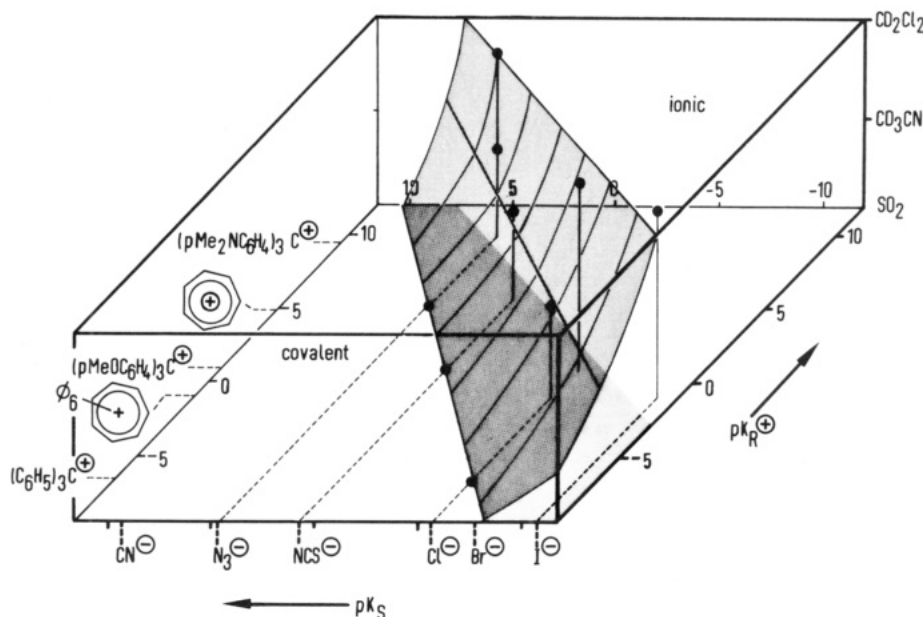(15) D. A. Kleier and G. Binsch, *QCPE*, **10**, 165 (1970).

Figure 2. Graphic search for systems in which ΔG° between ions and COV is small. Note that only compounds in the shaded area are possible to investigate by our method (see text).

Table I
Barriers of Ion Pair Recombination

system	R^+	X^-	solvent	T, K	$\Delta G_T^\ddagger$, kcal/mol	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	ref
1	$(C_6H_5)_3C$	Cl	SO_2/CD_2Cl_2 10:1	203	9.9^a	10.5^a	2.3^a	14
$1d_9$	$(C_6H_2D_3)_3C$	Cl	SO_2	203	9.7	11.3	8.1	14
2	$(MeOC_6H_4)_3C$	Cl	C_2H_3Cl/CD_2Cl_2 0.9:1	185	7.7^a			18
3	$(MeOC_6H_4)_3C$	NCS	SO_2/CD_2Cl_2 4.2:1	309	15.8	16.2	1.2	7
4	$(Me_2NC_6H_4)_3C$	N_3	CD_2Cl_2^{b}	235	11.5^a	11.7^a	1.1^a	18
5	C_7H_7	NCS	$CDCl_3/CD_3CN$ 1:3	243	$12.1^{a,c}$			19–21
			$CDCl_3$	298	$14.3^{d,e}$			21
			$CS_2/CDCl_3$ 10:1	298	$14.8^{d,e}$			21
6	C_7H_7	N_3	$SO_2/CDCl_3$ 4:5	232	10.3			20
					11.0^e	6.9^e	-18.3^e	22
			CD_3CN	298	$14.0^{d,f}$	$10.2^{d,f}$	$-12.4^{d,f}$	22
			$CDCl_3$	298	$14.6^{d,f}$			22
			THF	298	$15.6^{d,f}$			22

^{a} Pseudo-first-order evaluation. ^{b} 0.009 M. ^{c} Barrier COV → IP, 12.0 kcal/mol. ^{d} Migration of the ligand. The ion pairs are not detectable. ^{e} This barrier corresponds to COV → IP. ^{f} Overall rate evaluated. See ref 22.

The plot of K_{ion} vs. $(\gamma_\pm c_{COV})^{-0.5}$ gives as slope $(K_1K_2)^{0.5}$ and as intercept K_1. Whereas c_{COV} can be easy calculated from K_{ion} and the overall concentration, the values of $\gamma_\pm$ are more difficult to obtain. We have taken the Debye–Hückel approach to get the function $\gamma_\pm = f(c_{FI})$ and have used an iterative procedure to find out the initially unknown c_{FI}.[7,14]

The data treatment described above requires precise measurements of K_{ion} which are only available at temperatures below the coalescence of the NMR signals. The useful temperature range is very limited for trityl chloride in SO_2 due to freezing of the solvent (191–206 K). So, we get K_1 and K_2 values at these low temperatures but have no exact information about their temperature dependence. Nevertheless, the combination of our values with published K_1 and K_2 at 273 K derived from conductivity[16] and UV[17] measurements yields ΔH° and ΔS° for the two equilibria. Now, the energy profile exhibited in Figure 5 can be constructed.

Other Trityl Derivatives

The more stable tris(*p*-methoxyphenyl)methyl cation is interesting for two reasons. First, it was possible to measure ion pair recombination rates with two different anions, Cl^{-}[18] and NCS^{-}[7] (systems 2 and 3, Table I). Naturally, due to the $\Delta G^\circ \rightarrow 0$ condition, we had to choose different solvents. Second, the exceptionally high barrier for NCS^- together with the strong temperature dependence of the equilibrium enabled us to study directly the ionization process COV → ions in solution.[7] For this purpose, the sample tube was rapidly chilled to about 200 K and the changing signal inten-

(16) N. N. Lichtin, *Prog. Phys. Org. Chem.*, 1, 75 (1963).
(17) Y. Pocker, *Proc. Chem. Soc. London*, 386 (1959).
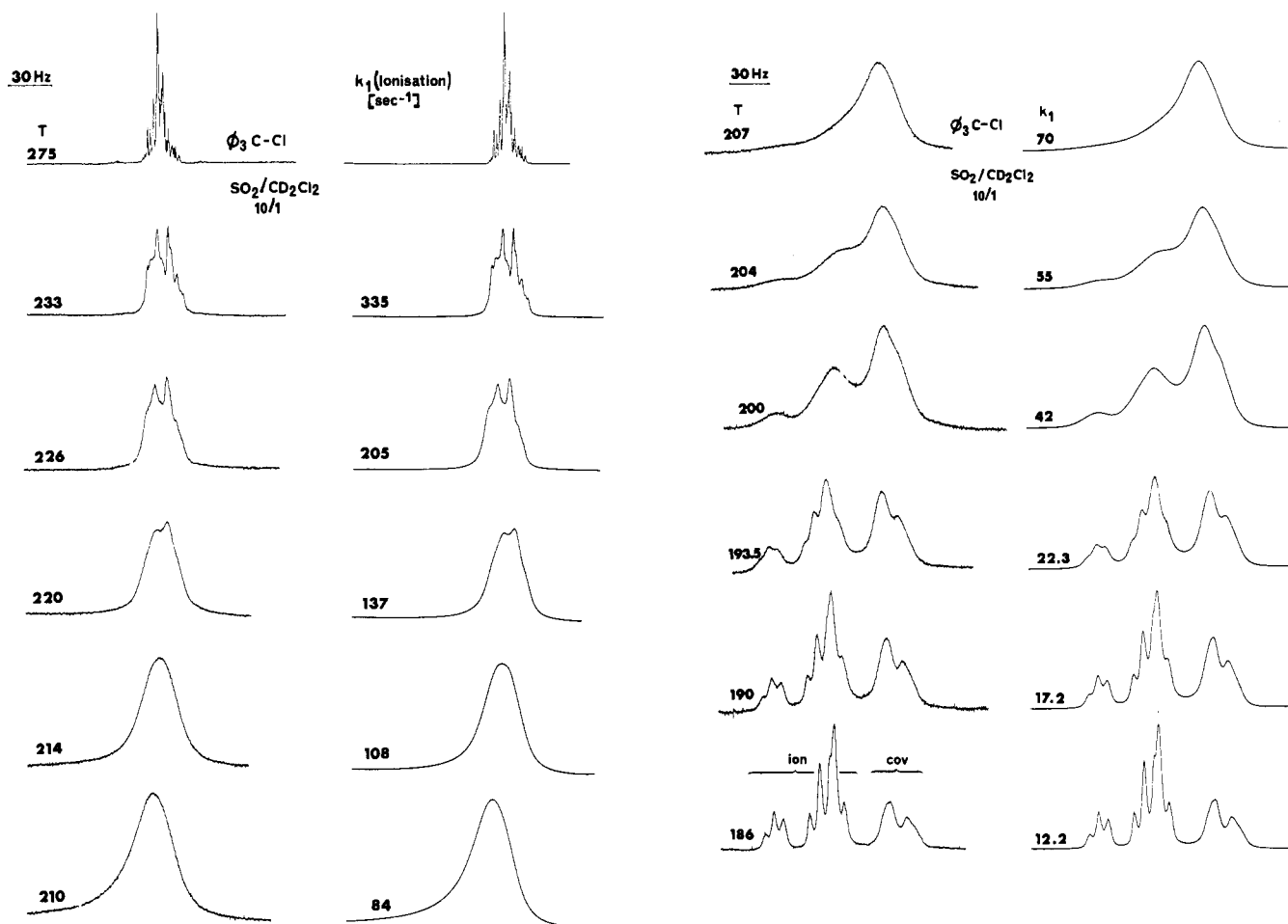(18) M. Feigel, Dissertation, Frankfurt, 1978.

Figure 3. Experimental (left) and calculated (right) 90-MHz ^{1}H NMR line shapes for trityl chloride in SO_2/CD_2Cl_2 10:1. $c = 0.07$ mol/L.

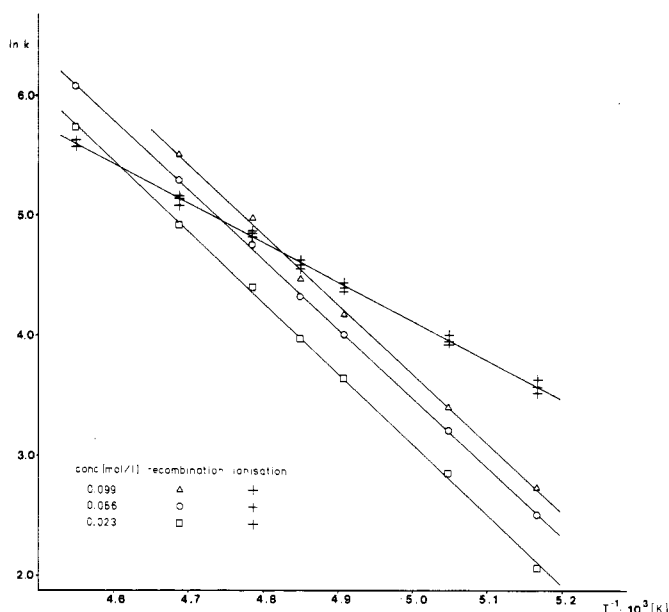**Figure 4.** Arrhenius plot for the rates of ionization (k_1) and overall recombination of the ions (k_{-i}) in system 1.

Figure 5. Energy profile for trityl-d_9 chloride in SO_2 at 203 K. The inclusion of the entropy data ($T\Delta S$) directly indicates the relative free energies ΔG. Compare the quite different shape of the profile for the same compound in a solvent of lower polarity in Figure 1.

sities (Figure 6) were evaluated. The combination of line-shape data with the results of this direct equilibration experiment yielded rate constants over a temperature range of more than 100 K and consequently very accurate activation parameters.

As the cation is further stabilized, the tris(4-dimethylaminophenyl)methyl cation requires the even
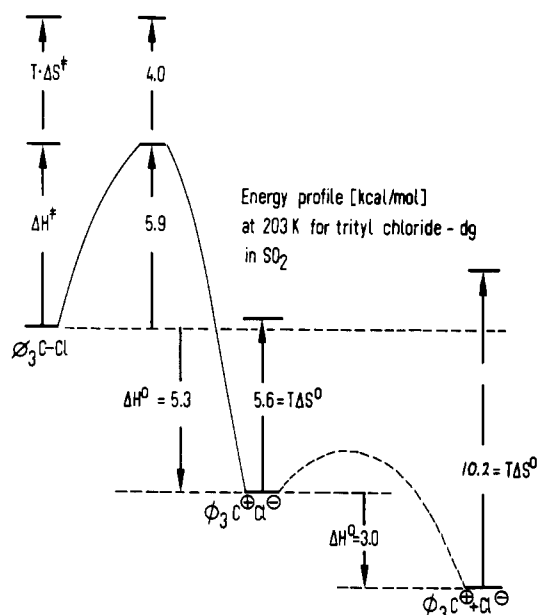
more strongly nucleophilic azide anion (N_3^-) for the equilibration in CD_2Cl_2 to be observable. Again a substantial barrier for the process RX $\rightleftharpoons$ R$^+$X$^-$ was observed (system 4, Table I).
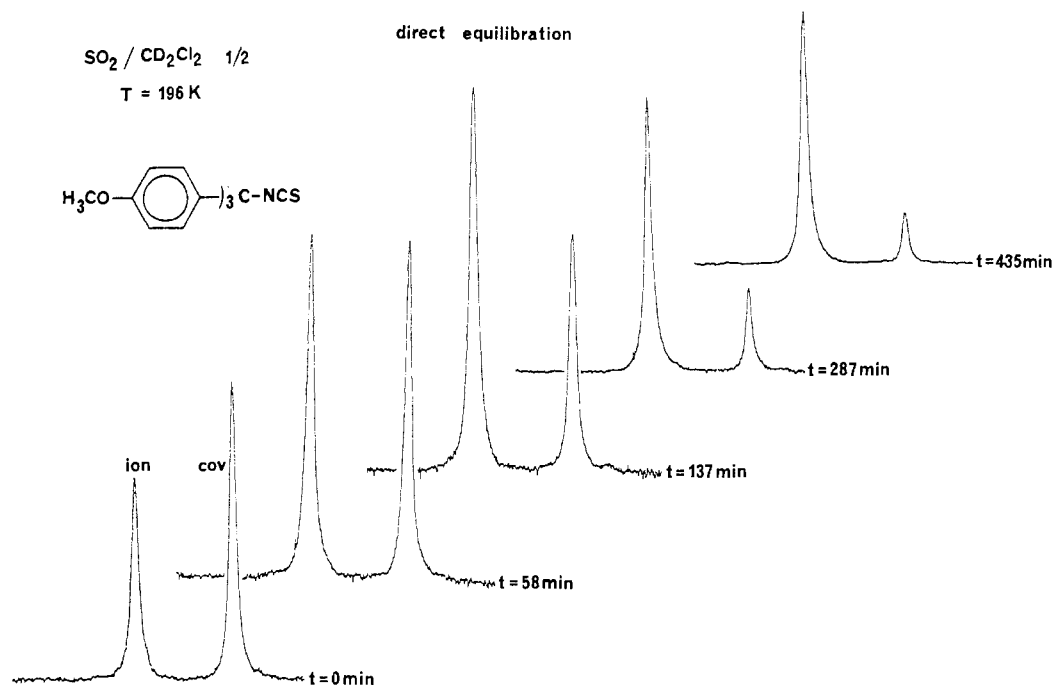
Figure 6. Direct equilibration of the process RX → R⁺X⁻ in system 3 (see text).

Table II
Solvent Dependence of the Free Activation Enthalpy $\Delta G^{\ddagger}_{298}$ (kcal/mol) for the
Migration of the Azide Group in Tropyl Azide

solvent	nucleus	Σ	1,2	1,3	1,4
CD₃CN	¹H	13.97 ± 0.02	14.7 ± 0.1	14.32 ± 0.04	15.2 ± 0.1
	¹³C	14.3 ± 0.1	14.8 ± 0.2	14.6 ± 0.2	16.0 ± 0.5
CDCl₃	¹H	14.6 ± 0.3	15.2 ± 0.5	14.9 ± 0.6	17.0
THF	¹³C	17.7 ± 0.2	16.5 ± 0.4	15.9 ± 0.4	17.0 ± 1

Ionization of 7-Substituted Cycloheptatrienes

Actually, the tropylium systems represent the compounds with which we began.[19,20] The solubility of tropylium chloride in solvents of low polarity was insufficient to provide any NMR signals. In polar solvents, only the ionic form of this compound is detectable. However, chlorotropylium chloride[10] is quite soluble, even in CS₂/toluene. In this solvent system only migration of chlorine in the covalent form was observed. Changing to more polar solvents caused the population of the ions to increase, but we were not able to freeze the equilibrium COV ⇌ IP. We got better results when we used tropylium isothiocyanate in CD₃CN[21] and the azide in SO₂/CDCl₃[22] (system 5, Table I).

Other Systems with Indirect Ion Pair Recombination Barriers

Numerous measurements of ionization rates in typical S_N1 reactions have been made, but barriers to ion pair recombination have seldom been estimated under equilibrium conditions. For the exchange reaction

$$R-X + R'^+ \rightleftharpoons R^+ + R'-X$$
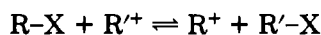
the DNMR spectra yield directly the ionization rate of R–X. Having also information about the stability of the ion pairs, Freedman et al. were able to calculate the ion pair recombination rate constant.[23] In that manner, NMR and UV data concerning tri-*p*-tolylmethyl chloride in CD₂Cl₂ allowed the ion pair recombination barrier to be estimated as 7.9 kcal/mol.[23]

In contrast, from study of mixtures of the phosphorane CH₃P(OC₆H₅)₄ with the corresponding cation CH₃P(OC₆H₅)₃⁺, a diffusion-controlled recombination rate was estimated.[24] In that study the amount of ions was estimated from the conductivity, and consequently the very fast recombination rate, which was measured in a solvent of low polarity (CD₃CN), evidently refers to combination of the free ions to form the ion pair (see above and Figure 1). Further complications can arise if proton transfer steps are involved in the equilibrium.[25,26]

Sigmatropic Shifts and Ionization

Species such as the tropylium and cyclopropenylium cations, in which ionization and recombination can lead to positional topomers, allow DNMR studies of ligand migration without requiring the direct observation of ionic species. From the dependence of the migration rate on solvent polarity an ionic pathway has often been

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(20) H. Kessler and A. Walter, *Angew. Chem.*, **85**, 821 (1973); *Angew. Chem., Int. Ed. Engl.*, **12**, 773 (1973).

(21) M. Feigel, H. Kessler, and A. Walter, *Chem. Ber.*, **111**, 2947 (1978).

(22) M. Feigel, H. Kessler, D. Leibfritz, and A. Walter, *J. Am. Chem. Soc.*, **101**, 1943 (1979).

(23) H. H. Freedman, A. E. Young, and V. R. Sandel, *J. Am. Chem. Soc.*, **86**, 4722 (1964).

(24) C. L. Lerman and F. H. Westheimer, *J. Am. Chem. Soc.*, **98**, 179 (1976); D. I. Philips, I. Szele, and F. H. Westheimer, *ibid.*, **98**, 184 (1976).

(25) J. I. Brauman and W. C. Archie, *J. Am. Chem. Soc.*, **92**, 5981 (1970).

(26) H. Blumenstock, F. Dickert, and A. Reichenbacher, *Z. Phys. Chem.*, **113**, 199 (1978).
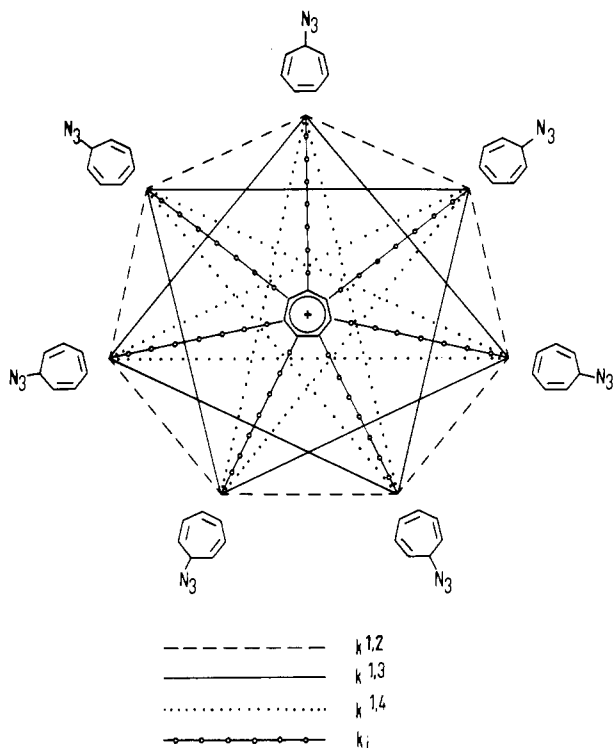
Figure 7. Isomerizational graph of the different rate processes in tropylium azide (6).

deduced.[27,28] The tropylium system, as compared to the cyclopropenylium system, has the advantage of allowing differentiation between selective migration and random walk processes. This is possible by means of saturation transfer experiments or line shape simulations of the ^1H and ^{13}C NMR spectra.[22] The high sensitivity of the line shape to the migration pathway allows an analysis of the rather complex kinetic process to be made (Figure 7). The NCS shift in tropyl isothiocyanate (system 5) is a random process,[21] but a preferred 1,3 shift of the azide was found in tropyl azide[22] (system 6), although ionization was observed in both cases in more polar solvents (see above). It is interesting to see the solvent dependence of the selective azide migration (Table II).

The barriers of all processes decrease as solvent polarity increases. This generalization is valid even for the selective 1,3 migration. This process is best interpreted as a 3,3-sigmatropic shift (hetero-Cope rearrangement) inasmuch as exchange of the terminal nitrogens of the azide occurs at a rate that is comparable to that of the walk around the 7-membered ring. It was possible to study this process by ^{15}N DNMR measurements.[18,29] The transition state of this Cope rearrangement, in which the two 3-atomic parts differ strongly in the electronegativity of the elements (C, N), should be considered as rather polar. The different migrational pathways differ in their sensitivity to solvent polarity. With increasing solvent polarity, the 1,2 shift becomes more important (26% in THF, 34% in CD_3CN). From the mechanistic viewpoint the latter

General Comments

process can represent a sigmatropic 1,7 shift with inversion of the nitrogen, or a least motion process via ions.

We have been able to study barriers to the recombination of ion pairs to covalent molecules in a number of systems. In one case (tropylium isothiocyanate in CD_3CN) we found strong evidence (charge-transfer UV band, chemical shift arguments) that the ion pairs exist predominantly as intimate ion pairs.[21] Carefully selected conditions (stability of the ions, solvent, temperature) are necessary in order to fulfill the DNMR requirements ($\Delta G° \sim 0$). Thus, it was impossible to vary only one of the above-mentioned parameters at a time. For instance, we can measure the recombination rate of a given cation with different nucleophiles (anion/solvent systems 2 and 3, Table I), but in the case of a less stable cation the same set of nucleophiles cannot be used. We are thus unable to prove either the occurrence of reactivity–selectivity relationships[30] or their breakdown.

Ritchie's N_+ correlation predicts the absence of reactivity–selectivity rules for cation/anion combination, starting with the separated ions.[2,31] The interpretation is still not clear, but it seems that the part played by the solvent, when two ions come together, has long been underestimated.[32] We hope that activation parameters for ion *pair* recombination will provide additional arguments that can be raised in this discussion.

One might mention that our observation of high barriers follows directly from the Hammond postulate:[33] the requirement of stable ions leads to an earlier transition state for the ionization. This is obviously correct, but we should also mention that we always observed comparable entropy values for the transition state and the ion pair; e.g., for system 1, $\Delta S^\ddagger = -19.7$ eu, $\Delta S° = -27.9$ eu; for system 3, $\Delta S^\ddagger = -11.5$ eu, $\Delta S° = -12.7$ eu; for system 4, $\Delta S^\ddagger = -12.3$ eu, $\Delta S° = -13.4$ eu.[18] The entropy values are mainly determined by the better solvation of the more polar ions. Consequently, we think that the solvation sphere of the transition state is in the systems 3 and 4 as rigid as it is in the ion pair.

Some additional freezing of solvent molecules has to occur in the triphenylmethyl chloride ion pair (system 1). Alternatively, the data can be explained by the following:[34] The ion pairs are in general more strongly solvated than the transition state of the ionization and therefore they have a lower entropy. This appears to be the case for triphenylmethyl chloride. The linear NCS^- and N_3^- ions in systems 3 and 4 undergo rotational and positional motions in the ion pair, which are hindered in the transition state. The additional entropy for these motions increases the entropy of the ion pair in 3 and 4, up to the value of the transition state.

A decision between the two arguments appears not to be possible based on the limited number of compounds studied. Once again, one should keep in mind that we have unavoidably changed cation and solvent in comparing systems with different anions. At present,

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(28) C. E. Wulfman, F. Yarnell, and D. S. Wulfman, *Chem. Ind. (London)*, 1440 (1960); D. S. Wulfman, L. J. Durham, and C. E. Wulfman, *ibid.*, 859 (1962); D. S. Wulfman and J. J. Ward, *Chem. Commun.*, 276 (1967).

(29) See footnote 29 in ref 22.

(30) A. Pross, *Adv. Phys. Org. Chem.*, 14, 69 (1977).

(31) C. D. Ritchie, *Pure Appl. Chem.*, 50, 1281 (1978).

(32) C. D. Ritchie, *Pure Appl. Chem.*, 51, 153 (1979).

(33) D. Farcasiu, *J. Chem. Educ.*, 52, 76 (1975).

(34) These arguments have been suggested by Professor J. F. Bunnett, University of California, Santa Cruz.

we can only state the following: On the entropy scale, the transition state for the ionization looks more like an ion pair with a rigid solvent shell than like the mildly solvated covalent form.

In retrospect, the existence of high barriers is not surprising, because increasing the bond distance of a molecule to form ions requires a good deal of energy, which has to be compensated by the better solvation of the more polar form (IP). Solvation provides large amounts of energy; a direct and optimal compensation is not possible for all geometries. Thus appreciably high barriers between COV and IP can exist.

Our method for measurements of ionization barriers requires at least a 5% participation of ionic forms in equilibrium with the covalent form. Due to this restriction no data are available for less stable ion pairs. Certainly, following the Hammond postulate, the barrier from ion pairs to covalent molecules in solution should decrease with decreasing stability of the ion pairs, but in our opinion the assumption of diffusion-controlled recombination of ions, which is often stated in the literature, seems not to be correct with respect to the conversion of ion pairs to covalent molecules.

The formation of ion pairs in protic solvents should be different. Also, heterolysis of a protonated, cationic species requires a smaller change in solvation than does ionization of a neutral one. Our measurements do not give information about barriers to ionization or ion pair recombination in protic solvents.