Direct Determination of the Lifetime of Ion Pairs in Solutions of Trimethylammonium Salts at a Low Temperature

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The interaction of strong acids with organic compounds in slightly polar aprotic solvents leads in the first place to the formation of close ion pairs with an interionic hydrogen bond ([1], [2], [3]). The lifetime of an individual ion pair $A^-\ldots HB^+$ in solution may be limited by several elementary processes:
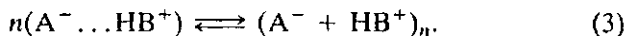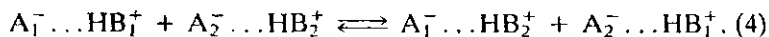
1. Dissociation into free molecules of acid and base:

$$A^-\ldots HB^+ \rightleftharpoons AH + B. \qquad (1)$$

2. Dissociation into free solvated ions:

$$A^-\ldots HB^+ \rightleftharpoons A^- + HB^+. \qquad (2)$$
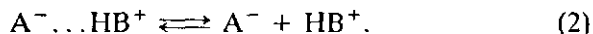
3. Association with the formation of polymeric **neutral** (as a whole) complexes:

$$n(A^-\ldots HB^+) \rightleftharpoons (A^- + HB^+)_n. \qquad (3)$$

4. Ion exchange:

$$A_1^- \ldots HB_1^+ + A_2^- \ldots HB_2^+ \rightleftharpoons A_1^- \ldots HB_2^+ + A_2^- \ldots HB_1^+. \quad (4)$$

Here A_1H, A_2H, B_1, and B_2 are identical or different acid and base molecules. The ion exchange (4) may simply involve the successive steps of dissociation (1) and (2) and formation of ion pairs, but it may also be a true double exchange reaction proceeding, for example, in a bimolecular complex of reacting ion pairs.

At room temperature the lifetimes of ion pairs in solution are too short to be measured by NMR. Thus, the NMR spectra of solutions containing two salts (e.g. $R_3NH^+ \cdot X^-$ and $R_3NH^+ \cdot Y^-$) show only one averaged signal of the NH proton. Our attempts to measure the time to equilibrium (4) with rapid mixing of the solutions of the two salts employing the stopped-flow technique with recording being made from the IR absorption in the milli-second time range failed; this means that the bimolecular rate constant of the ion exchange is higher than 10^5 liter·mol^{-1}·s^{-1}. The only estimate of this constant known to us ($k = 6.5 \times 10^7$ liter·mol^{-1}·s^{-1} at 26°C for dialkylanilinium acetates) has been obtained [4] indirectly in an analysis of the kinetics of proton exchange between OH^- and NH^+ groups in glacial acetic acid.

In this work we made an attempt to determine directly the lifetimes of ion pairs by using the dynamic NMR method at a low temperature in liquefied gases. The objects chosen for our investigations are the salts of trimethylamine $(CD)_3{}^{15}N$ with trifluoroacetic acid, CF_3COOH, and with 2, 4, 6-trichlorophenol. The use of the given isotope modification permits one to avoid the effect of quadrupole relaxation of the nitrogen nuclei on the linewidth of the NH proton; the presence of a spin-spin coupling with the nucleus ^{15}N permits one to assess the possible contribution of the proton exchange to the contour shape. The preparation and purification of the amine sample used in this work are described in Ref. [5]. The crystalline salts were prepared by passing a small excess of the amine into a solution of the acid in ether at $-30°C$. The salts were recrystallized from the ether-dichloromethane mixture, after which they were dried for a long time in a vacuum of 10^{-4} torr. All the operations were carried out in a vacuum setup, without any contact with air. The solvent used was a mixture of freons, $CDF_3 + CDF_2Cl + CDFCl_2$ (3:4:1), which is a low-viscosity liquid up to 80 K. The solubility of the salts studied in this mixture at 85 K was not worse

than 0.1 mol/liter. The procedure for working with solutions in liquefied gases is described in the literature ([6] and [7]). The ^1H NMR spectra were taken using a Jeol C-60 HL spectrometer (60 MHz). The accuracy of thermostatic control in the range $80-100$ K was about $\pm$ 1 K.

The signal of the NH^+ proton in the NMR spectrum of the solution of trimethylammonium trichlorophenate is a doublet with δ = 13.5 ppm and J_{NH} = 75 Hz. (The chemical shifts were measured with respect to TMS.) The values of δ and J are practically independent of the temperature in the range $85-150$ K and of the concentration in the range $(1-7) \times 10^{-3}$ mol/liter. This means that under the given conditions the solution mainly contains monomeric ion pairs with the proton being completely transferred to the nitrogen atom. (The presence of association (3) is responsible for the temperature and concentration dependence of the chemical shift [8], and the reversible proton transfer inside the complex $A^-...HB^+$ $\rightleftharpoons$ AH...B leads to a temperature dependence of both the chemical shift and the effective value of J_{NH}[9].) Since the lines of the doublet are narrow, the proton exchange under the conditions indicated proceeds at an immeasurably low rate. The signal of the NH^+ proton in the NMR spectrum of the solution of trimethylammonium trifluoroacetate is analogous, its spectroscopic parameters being δ = 11.2 ppm and J_{NH} = 78 Hz.

The spectra of the solution containing the two salts are shown in Fig. 1. At 85 K, two unbroadened doublets are observed, which belong to the trimethylammonium cation in ion pairs with trichlorophenate and trifluoroacetate anions (hereafter these anions are denoted by X and Y). When the solution is heated, the lines are broadened and the doublet structure becomes blurred, this being followed by the collapse of the signals. In the $140-170$ K range the spectra show one well-resolved doublet, whose position depends on the relative concentration of the two salts. The fact that the doublet structure of the averaged signal is retained indicates that the collapse of the signals is caused by the ion rather than the proton exchange (the ion exchange cannot proceed through dissociation into free molecules (1)).

The lifetimes of the ion pairs, τ_X and τ_Y, were determined by analysis of the full contour of the merging signals. The experimental contours were compared by the least squares method with the
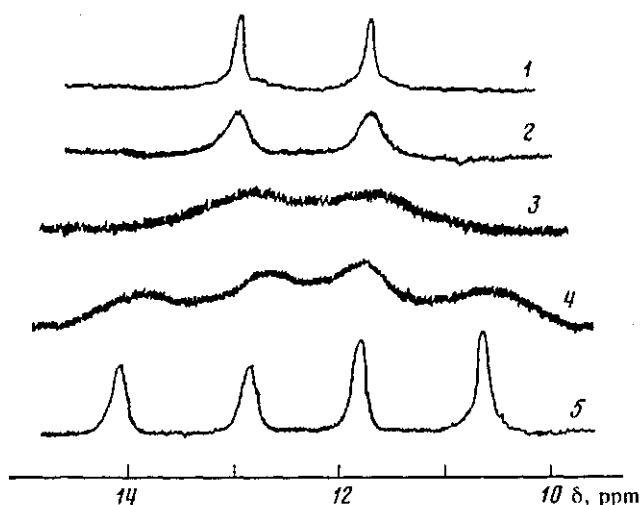
FIGURE 1   The ^{1}H NMR spectra of a solution containing 4×10^{-3} mol/liter of salt X and 5×10^{-3} mol/liter of salt Y in a mixture of freons at temperatures: (*1*) 135, (2) 120, (*3*) 116, (*4*) 103, (*5*) 85 K.

theoretical contours constructed on a computer [10]. In constructing the spectra only one parameter was varied, namely the average lifetime $\tau = 1/2\,(\tau_X + \tau_Y)$, and the others were determined experimentally. The chemical shifts δ_X and δ_Y and the line half-widths in the absence of ion exchange, T_{2X}^{-1} and T_{2Y}^{-1}, were obtained from the spectra of solutions containing only one component X or Y at a given temperature. The relative concentrations of the forms p_X and p_Y were determined when proportioning the salts and checked by the chemical shift of the averaged signal: $\delta = p_X\delta_X + p_Y\delta_Y$.

An analysis of the concentration dependence of the lifetimes thus obtained shows that the exchange reaction is first order in each of the components. As an example, Fig. 2 shows the dependence of the logarithm of the lifetime, $\ln\tau_X$, on the logarithm of the absolute concentration of component Y at various temperatures (the concentration c_Y was varied from 2×10^{-3} to 5×10^{-2} mol/liter; the concentration c_X was fixed at 5×10^{-3} mol/liter). The slope of the straight line is close to unity; the intercept on the ordinate gives the value of the logarithm of the bimolecular rate constant of the ion
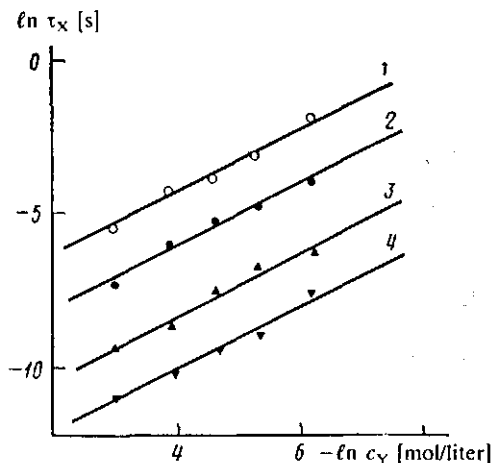
FIGURE 2 Dependence of the lifetime of ion pair X on the concentration of ion pair Y at temperatures: (*1*) 90, (2) 100, (3) 120, (4) 140 K.

exchange k. At 150 K the value of the rate constant $k = 2.4 \times 10^6$ liter·mol^{-1}·s^{-1}; extrapolation to room temperature gives the value 2.6×10^8 liter·mol^{-1}·s^{-1}. The activation energy of the reaction is $E^* = 2.8 \pm 0.3$ kcal/mol; the entropy of activation $\Delta S = -8.4$ eu. These characteristics show that the ion exchange cannot be realized via a dissociative route, namely, through step (2) of formation of free ions. Indeed, the separation of ions, for example, in a medium with $\varepsilon = 3$ (ε is the dielectric constant) requires an energy of about 30 kcal/mol. The concentration dependences of the lifetimes suggest that the exchange occurs in the bimolecular cyclic complex of ion pairs by way of simultaneous (cooperative) rotation of the B_1—H and B_2—H bonds through 90° in opposite directions, this leading to the displacement of the hydrogen bonds.

Such symmetric dimers of ion pairs ("ion quadrupoles") have actually been detected from the IR absorption spectra in solutions of the salts R_3NH^+·Hal$^-$ (Hal = Cl, Br, I) in nonpolar solvents ([11] − [14]). Moreover, it has been found that the degree of association of ion pairs sharply decreases with increasing volume of the ions and also with increasing dielectric constant of the solvent. Thus, the IR spectra obtained by the present authors for solutions of the salts of complex organic acids with amines (in particular, the
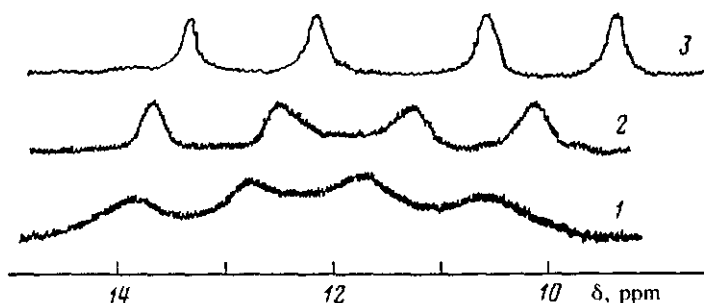
FIGURE 3 The ^{1}H NMR spectrum of solutions containing salts X and Y (*1*) and additions of butyronitrile [(2) 0.05 mol/liter, (3) 0.2 mol/liter].

salts X and Y) in $CHCl_3$ or in a mixture of freons do not betray any presence of appreciable concentration of ion quadrupoles. However, it may be presumed that such dimers do exist as short-lived intermediates of the ion exchange reactions. This is confirmed indirectly by the fact that the NMR spectra of solutions containing both trimethylammonium hydrochloride and hydrobromide exhibit, down to the lowest temperatures, a single averaged doublet of the NH^+ protons, whose position depends strongly on temperature and concentration. This means that the ion exchange is sharply accelerated in cases where the degree of association of ion pairs is high.

It has been found [11], [12] that addition of molecules with a high dipole moment (such as nitriles) to a solution of the salt in a nonpolar solvent leads to the breakdown of ion quadrupoles and the formation of analogously built complexes by electrostatic interaction:
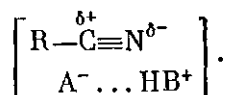
$$\left[\begin{array}{c} R - \overset{\delta+}{C} \equiv N^{\delta-} \\ A^- \ldots HB^+ \end{array} \right].$$

Figure 3 shows the variation in the spectra of a solution (at 103 K) containing the salts X and Y in concentrations of 5×10^{-3} mol/liter, upon addition of butyronitrile, C_3H_7CN ($\mu = 3.57$ D). The two signals shift to a strong field, which corresponds to the shift of the equilibrium to the formation of complexes of ion pairs with the nitrile. The lifetimes of such complexes are short on the time scale of NMR even at 80 K, and therefore no individual signals of the

monomers $A^-...HB^+$ and the complex are observed. The shift of the signals is accompanied by the appearance of a spin-spin structure and the narrowing of the doublet lines, which points to a decrease in the rate of the ion exchange. It will be logical to presume that the cause for the slowing-down of the ion exchange is the breakdown of the bimolecular intermediate complexes formed in the reaction.

Thus, it may be concluded that the lifetime of an individual ion pair in slightly polar solvents is determined by a cooperative ion exchange that presumably occurs in dimers bound by electrostatic forces.

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