

INTERACTION OF AMMONIUM SALTS WITH PROTON
DONORS IN SOLUTION*

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According to the results of physicochemical analysis, ammonium salts exist in solvents of low dielectric constant as strongly associated ion pairs. In previous studies [1, 2] the effects of this association on the IR spectra and NMR spectra of solutions of trialkylammonium salts have been described. With formation of the ion pairs of dimers and of higher aggregates the $\nu(\text{NH})$ band is shifted discretely to the high frequency region. This shift has been observed when trialkylammonium halides interact with other molecules, which possess a significant dipole moment, the magnitude of the shift increasing with rise in the dipole moment of the molecule-partner. Analysis of the spectroscopic data suggests the existence in solution of dipole-dipole type complexes [1, 3].

In the present work the interaction of trialkylammonium halides R_3NHHal ($\text{R} = \text{C}_8\text{H}_{17}$, $\text{C}_{10}\text{H}_{21}$, $\text{Hal} = \text{Cl}$, Br) with molecules of the proton donors CH_3OH , $\text{iso-C}_4\text{H}_9\text{SH}$ and CHCl_3 in CCl_4 solution has been studied. The results of earlier studies [4-6], in which the IR spectra were measured in the region of the $\nu(\text{OH})$ and $\nu(\text{CH})$ bands, of solutions of alcohol and chloroform in the presence of ammonium salts showed that these molecules form hydrogen bonds with the anions of the salts. Investigation of the effects of these bonds on the $\nu(\text{NH})$ bands of the cation in the ion pairs provides additional information characterizing the intermolecular interaction in which the ammonium salts in the solutions participate. The study was carried out in the $1800\text{--}2800\text{ cm}^{-1}$ region on an IKS-12 spectrometer with an LiF prism.

In Fig. 1 are shown the spectra of 0.0075 moles/liter solutions of tridecylammonium chloride in CCl_4 containing 0.075 and 0.75 moles/liter alcohol and 0.75 moles/liter chloroform. The $\nu(\text{NH})$ band of the tridecylammonium chloride solution with two maxima at 2050 and 2300 cm^{-1} ascribed to monomeric and dimeric salt molecules [1] noticeably changes its position and shape in the presence of proton donor molecules. The $\nu(\text{NH})$ band undergoes the largest shift, compared with the shift on formation of a dipole-dipole complex with a molecule of a tetraalkylammonium salt, in the presence of methanol, which was the most active medium of the donors studied. Interaction with chloroform leads to a much smaller shift of the $\nu(\text{NH})$ band, compared with the shift caused by formation of the dipole-dipole complex with acetonitrile. In the presence of 0.05 and 0.5 moles/liter iso-butylmercaptan the appearance of the $\nu(\text{NH})$ band hardly changes. This could be due not only to a small shift in value of the $\nu(\text{NH})$ band on formation of the $\text{SH}\dots\text{Cl}^-$ hydrogen bond, but also to a low concentration of the complexes with this bond. Since the dipole moments of the donor

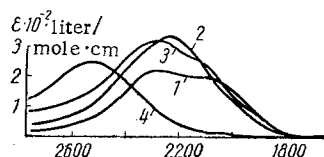


Fig. 1. Spectra of $(\text{C}_{10}\text{H}_{21})_3\text{NHCl}$, 0.0075 moles/liter solution in: 1) CCl_4 and in CCl_4 containing 2) 0.75 moles/liter CHCl_3 ; 3) 0.075 moles/liter CH_3OH , and 4) 0.75 moles/liter CH_3OH .

molecules are not very large (1.65; 1.2 and 1.4 D for CH_3OH , CHCl_3 and $\text{iso-C}_4\text{H}_9\text{SH}$) and there is no correlation between the values of the frequency shift and the dipole moment of the partner, it can be inferred that the observed changes in the spectrum are caused, mainly, by formation of the $\text{X-H}\dots\text{Hal}$ hydrogen bond. The increase in the frequency $\nu(\text{N}^+\text{H}\dots\text{Cl}^-)$ on formation of the hydrogen bond can be explained by a shift in the electron cloud of the anion towards the proton donor and by a decrease in the electron density at the $\text{N}^+\text{H}\dots\text{Cl}^-$ bond. This results in a weakening of the $\text{N}^+\text{H}\dots\text{Cl}^-$ bond and to an increase in the $\nu(\text{NH})$ frequency.

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TABLE 1

Compound	CH ₃ OD (10 ⁻² M)		iso-C ₄ H ₉ SD (5 · 10 ⁻² M)	
	τ _{1/2} , sec	k, 1/ M · sec	τ _{1/2} , min	k, liters/ M · sec
R ₃ NHCl				
10 ⁻³ , M	2	30	—	—
5 · 10 ⁻³ , M	—	—	5	4,2 · 10 ⁻²
R ₃ NHBr				
10 ⁻³ , M	6	10,5	—	—
5 · 10 ⁻³ , M	—	—	10	2,1 · 10 ⁻²
R ₃ NHJ				
10 ⁻³ , M	10	6,3	—	—
5 · 10 ⁻³ , M	—	—	11	1,9 · 10 ⁻²

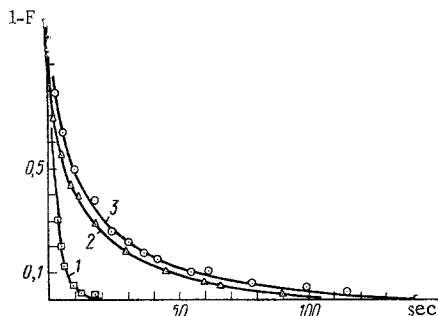
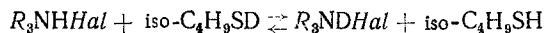
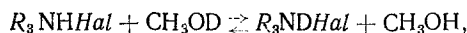


Fig. 2. Kinetic curves for the hydrogen exchange reaction: 1) Oct₃N · HCl (10⁻³ mole/liter); 2) Oct₃NHBr (10⁻³ mole/liter) + CH₃OD (10⁻³ mole/liter); 3) Oct₃NHJ (10⁻³ mole/liter). Solvent CCl₄.

We noted that with an excess of the proton donor in solution the anion could combine with more than one donor molecule. This, apparently, explains the difference between the spectra of tridecylammonium chloride with a tenfold and a hundredfold excess of methanol in CCl₄. In solutions of trioctylammonium chloride in pure CHCl₃ on decreasing the salt concentration no band appeared which, as in the case of solutions in CCl₄, could be ascribed to a monomer ion pair, and it was not possible to observe spectroscopically the dissociation of the salt into monomer molecules. The unusual feature of chloroform as a solvent lies in the fact that formation of a hydrogen bond of the anion of the salt with the CH group of the chloroform leads to a shift of the ν(NH) band of the cation to the high frequency region, with approximately the same value as the low frequency shift of the ν(NH) band, which arises during dissociation of the dimer salt molecules.

The spectra of trialkylammonium bromide and iodide in the presence of CH₃OH, CHCl₃, iso-C₄H₉SH change in a similar way. The shift of the ν(NH) frequency due to formation of a hydrogen bond with the anion decreases in the series Cl⁻, Br⁻, I⁻ corresponding to the decrease in proton-acceptor ability of the anions in the series. Whereas the increase in the frequency of the chloride monomer at 2050 cm⁻¹ for a hundredfold excess of methanol is 450 cm⁻¹, the band of the bromide monomer at 2250 cm⁻¹ shifts 350 cm⁻¹ at a 0.005 moles/liter salt and 0.5 moles/liter alcohol content and the band of the monomer iodide at 2450 cm⁻¹ shifts 150 cm⁻¹ at the same concentrations of salt and alcohol.

Additional information about the interaction between proton donors and ammonium salts in solution is provided by the results of a study of the rate of exchange of the hydrogen of the NH group of the salt and the OH or SH group of the donor. The kinetics of the reactions



were followed in CCl₄ solution by the change in the intensity of the ν(NH) band of the salt after addition to a solution of a deuterium donor. The experiments were carried out in glass absorption cells with CaF₂ and LiF windows. In Fig. 2 are depicted the kinetic curves for hydrogen exchange of the trialkylammonium halides with D-methanol. Along the abscissa is plotted the function 1 - F = (D_t - D_∞) / (D₀ - D_∞), where D₀, D_t, D_∞ are the optical densities of the ν(NH) band at the initial moment of time, at time t, and after an equilibrium distribution of isotopes has been established. The process obeys the exponential law

$$[\text{NH}]_t = [\text{NH}]_\infty + ([\text{NH}]_0 - [\text{NH}]_\infty) e^{-rt},$$

and the experimentally measured value of r is connected with the rate of isotopic exchange by the ratio

$$R = r \left(\frac{1}{[\text{NH}] + [\text{ND}]} + \frac{1}{[\text{OH}] + [\text{OD}]} \right)^{-1},$$

which is correct if the isotope effect is neglected.

From Fig. 2 it follows that the rate of hydrogen exchange between methanol and trialkylammonium halides is a maximum for the chloride which is decreased for the bromide and is still less for the iodide. Exchange with mercaptan proceeded at a rate approximately two orders of magnitude slower than with methanol, in agreement with the lower stability of the hydrogen bond formed by the sulfhydryl group compared with the hydroxyl group [7]. The rate of exchange with mercaptan, as for methanol, fell from the chloride, to the bromide, to the iodide. In Table 1 values are given for the half-exchange period and the reaction rate constants calculated assuming the process to be bimolecular.

The facts described above indicate that the rate of isotopic exchange of hydrogen between the molecule-partners is determined by the special features of their electron shell structure, which play a fundamental role in the hydrogen bond formation.

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LITERATURE CITED

1. G. S. Denisov, E. V. Ryl'tsev, and D. N. Suglovov, Dokl. Akad. Nauk SSSR, 164, 1093 (1965).
2. W. E. Keder, and L. L. Burger, J. Phys. Chem., 69, 3075 (1965).
3. G. S. Denisov, E. V. Ryl'tsev, and D. N. Suglovov, Optika i Spekr., 23, 628 (1967).
4. A. Allerhand, and P. R. Schleyer, J. Am. Chem. Soc., 85, 1233 (1963).
5. A. A. Lipovskii, and T. A. Dem'yanov, Radiokhimiya, 8, 112 (1966).
6. M. F. Retting, and R. S. Drago, J. Am. Chem. Soc., 83, 2966 (1966).
7. G. S. Denisov, É. M. Kazakov, and E. V. Ryl'tsev, Zh. Prikl. Spektroskopii, 8, 690 (1968).