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Nuclear Magnetic Resonance Spectra of Complexes of Hydrogen Halides with Trimethylamine in Gaseous Phase

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^1H NMR spectra of gaseous mixtures containing trimethylamine ^{15}N and hydrogen halides HCl, HBr, DCl and DBr have been recorded, each of the components being in more than a thousandfold excess, in the range of 250 to 350°C. Changes are found in the spectra of the mixtures (in comparison with the spectra of the individual components) that are caused by complex formation. Judging from its spectra characteristics (particularly, from the chemical shift and the spin-spin coupling constant of methyl protons), the complex $(\text{CH}_3)_3\text{N} \cdot \text{HCl}$ should be classified as molecular with a rather strong hydrogen bond; in the complex $(\text{CH}_3)_3\text{N} \cdot \text{HBr}$ a proton transfer with the formation of an ion pair takes place. The energies of these complexes in the gas phase are estimated: $\Delta H_{\text{HCl}} = 9.2 \pm 2$ kcal/mol and $\Delta H_{\text{HBr}} = 13.6 \pm 1.5$ kcal/mol.

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The possibility of proton transfer between uncharged molecules in the gas phase and the structure of the isolated complex formed by the molecules of a strong acid AH and a base B were discussed in a number of theoretical and experimental studies [1-16]. In [1, 2] the potential energy surface for a system of interacting molecules $\text{H}_3\text{N} + \text{HCl}$ was calculated by using a non-empirical version of the SCF-LCAO-MO method with an extensive set of basic functions and with due regard for the configurational interaction. The

surface had only one minimum (with a depth of ~ 19 kcal/mol) in the region of coordinates corresponding to an ion pair with the hydrogen bond $A^- \dots HB^+$.

The idea of "self-ionization" taking place for the interaction of isolated H_3N and HCl molecules was later on confirmed by calculations [3, 4] in which less extensive and flexible bases STO-3G and 4-31G were employed. Recently, however, the authors of [5] performed calculations for the same complex again. This time polarization functions of d -type, localized on the nitrogen and chlorine atoms were included into the basis. The result proved to be rather surprising: the optimal geometrical structure was found to correspond to the molecular complex, and the configurations of the interacting molecules appeared to be only slightly perturbed by the hydrogen bond $AH \dots B$. A shallow minimum of 9 kcal/mol on the potential energy surface corresponded to the weak hydrogen bond. If we take the estimate of the zero vibrational energy as given in [5], the enthalpy of the complex will be 5.9 kcal/mol only. Later on [6], complexes of HCl with stronger bases — CH_3NH_2 and $(CH_3)_2NH$, were calculated with the use of the basis 4-31G. The optimal geometrical parameters and the dipole moments ($\sim 10D$) of the complexes corresponded to typical ion pairs with energies of 18.2 and 21.7 kcal/mol respectively.

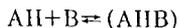
Nevertheless, the results reported in [5] and the discussion in [7] suggest that a cautious attitude should be taken toward the conclusions about the geometrical structure of relatively weak complexes, if such conclusions rest on the use of average bases into which polarization functions were not included. One has to admit that the nonempirical quantum-chemical calculations so far performed furnish no proof of "self-ionization" being possible for the interaction of isolated molecules of AII and B.

After the first nonempirical calculations for the complexes had been published, attempts were made to verify them experimentally. In a series of investigations [8-10], IR absorption spectra of HCl and HBr complexes with a number of proton acceptors B, isolated in a nitrogen matrix, were obtained. The basicity of B was inferred from proton affinity in values PA_B in the gas phase. As the basicity of B increased, the longitudinal vibration frequency

ν_s of the bridging proton sharply decreased to 700 cm^{-1} (for $H_3N \cdot HCl$); with a further increase of PA_B the frequency ν_s grew (1560 cm^{-1} for $(CH_3)_3N \cdot HCl$, 1870 cm^{-1} for $(CH_3)_3N \cdot HBr$). Complexes corresponding to the ascending branch of ν_s (PA_B) were interpreted as ion pairs with the proton transferred; in the extreme case of $H_3N \cdot HCl$, probably, a "quasi-symmetrical" hydrogen bond $A^{\delta-} \dots H \dots B^{\delta+}$ with a "fully shared proton" is realized. However, in [11, 12] attributing the above-mentioned bands to the longitudinal vibration of the proton was called in question, and not without reason. In our opinion, the structure of the complexes of hydrogen halides with ammonia and amines in a matrix cannot at present be regarded as finally established. Even a rigorous proof of proton transfer in a matrix does not signify that an ionic complex actually exists in the gas phase. It will obviously be unreasonable to make a direct comparison of the experimental data obtained for the condensed phase with the results of calculations performed for isolated complexes.

As far as we know, only three investigations [14-16] can be cited, in which complexes formed by strong acids and amines in the gas phase were studied experimentally. In [14] the existence of a stable molecule of $H_3N \cdot HCl$ in equilibrium with free HCl and H_3N was proved for the first time with the aid of high-temperature mass spectrometry. It was possible to estimate the bond energy ($10 \pm 2\text{ kcal/mol}$), but the structure of the complex (whether ionic or molecular) remained unclear. Later on [15] the IR spectrum of a complex of trimethylamine with trifluoroacetic acid (very strong in the gas phase) was successfully obtained. Proceeding from the presence of an intensive stretching vibration band of the $C=O$ group, shifted $\sim 30\text{ cm}^{-1}$ in comparison with the corresponding band of the free molecule of CF_3COOH , this complex must be classified as being typically molecular with a rather strong hydrogen bond. At the same time the IR and NMR spectra of this complex in aprotic nonpolar solvents [17-18], as well as its IR spectrum in a nitrogen matrix [19], prove convincingly a complete transfer of the proton and formation of an ion pair $A^- \dots HB^+$ have taken place. This fact shows clearly that it will be erroneous to draw conclusions about the structure of isolated complexes by reasoning from the data obtained in solvents, even if the latter are most "inert".

The main difficulty encountered in experiments directed at obtaining the spectra of complexes of $H_3N \cdot HCl$ type in the gas phase resides in a very low vapor pressure, associated with the high energy of the ion crystal lattice. At high temperatures, when the pressure of the complex vapors becomes measurable spectroscopically, the equilibrium



is strongly shifted to the left, so that one has to tackle the complicated problem of identifying the complex against the background of a tremendous excess of free AH and B molecules. Thus, according to the estimates presented in [14], the proportion of complexes in the vapors saturated at 300° over crystalline NH_4Cl does not exceed 0.01%. In the IR spectra of these vapors the authors of [15] could find no indications of complex formation. Our present work is an attempt to identify the formation of complexes between hydrogen halides and trimethylamine in the gas phase at temperatures ranging from 250 to $350^\circ C$, proceeding from 1H NMR spectra.

EXPERIMENTAL

Hydrogen halides HCl, HBr, DCl and DBr were prepared and purified immediately before the experiment by conventional methods [20]. Particular attention was paid to the removal of traces of water. Water was removed by carrying out successive operations of bubbling gases through a solution of P_2O_5 in orthophosphoric acid, then through a layer of an appropriate liquid hydrogen halide at a temperature close to its boiling point, this being followed by repeated low-temperature vacuum distillation, and, finally, by sublimation in a vacuum of 10^{-5} torr [20]. Isotopic modifications of trimethylamine $(CH_3)_3^{15}N$ and $(CD_3)_3^{15}N$ were prepared from $^{15}NH_4Cl$ (98% isotopic purity) and DCDO (99.5% isotopic purity) [21]. Desiccation of the amines was performed by passing them through a layer of zeolite 4A, then through a layer of calcium hydride, and after that the amines were subjected to low-temperature vacuum distillation.

At a temperature of $\sim 300^\circ C$ in gaseous mixtures of trimethylamine with

hydrogen halides irreversible chemical reactions proceed at a rather high rate; therefore no prolonged build-up of an NMR signal is possible. In our work we used a Jeol C-60 HL spectrometer with external stabilization, so that spectrum recording took only a few minutes. Minimum concentration of a gas the instrument could reliably detect with an optimum relaxation time (T_1 on the order of some fractions of a second) was $\sim 10^{-2}$ Amagat per proton. Such an order of magnitude was found to hold for concentration of saturated vapors of HCl complexes with trimethylamine over a salt melt at $\sim 300^\circ\text{C}$. In our experiments we used double, thick-walled glass ampoules of special design, whose volume was measured beforehand. These ampoules were so arranged that their entire internal volume was within the heated portion of the spectrometer transducer. The ampoules were sealed to the vacuum line and evacuated to 10^{-5} torr with heating to 300°C to remove the adsorbed molecules. After that metered quantities of the gases to be investigated were transferred into the ampoules and the latter were sealed. Metering was performed in terms of gas pressure in a measured volume; the gas pressure was measured with an accuracy of 3 to 5% with the aid of a sensitive element gas discharge pressure gauge VDG -1. For detecting changes in the spectrum of one of the components, caused by complex formation, the second component was taken in great excess (on the order of 1:1000), since only under such conditions the equilibrium (I) becomes sufficiently shifted to the right.

RESULTS

Spectra of gaseous mixtures of two types were obtained. In a first version, hydrogen halides HX with a concentration of $(4-8) \cdot 10^{-2}$ Amagat and deuterated trimethylamine $(\text{CD}_3)_3^{15}\text{N}$ with a concentration of 10-50 Amagat were placed into the internal ampoule. In this case the external ampoule contained the same quantity of HX and 20-30 Amagat of dry argon (to eliminate spectrum line broadening caused by the spin-rotational relaxation). At a temperature sufficiently high for the evaporation of the initially formed salt, two signals were observed in the spectrum, which were due to the molecules of HX in the external and internal ampoules. (With external stabiliza-

tion of the instrument this is the only way of identifying small shifts caused by complex formation with sufficient assurance.) Furthermore, a signal was seen, which was due to the remaining protons of the trimethylamine taken in tremendous excess; in the case of nondeuterated amine, weak signals due to HX could not be distinguished against the background of its absorption (in spite of a considerable difference in the chemical shifts).

In a second version, the internal ampoule contained $(2-4) \times 10^{-2}$ Amagat of trimethylamine $(\text{CH}_3)_3^{15}\text{N}$ and 10-50 Amagat of DX; the external ampoule contained the same quantity of trimethylamine and 20-30 Amagat of argon. At a high temperature, two signals belonging to the trimethylamine were observed along with the signals due to the remaining protons of DX. The spectra of gaseous mixtures of trimethylamine are presented in Figs. 1-3.

DISCUSSION

Figure 1 shows the spectra of the system trimethylamine-trimfluoroacetic

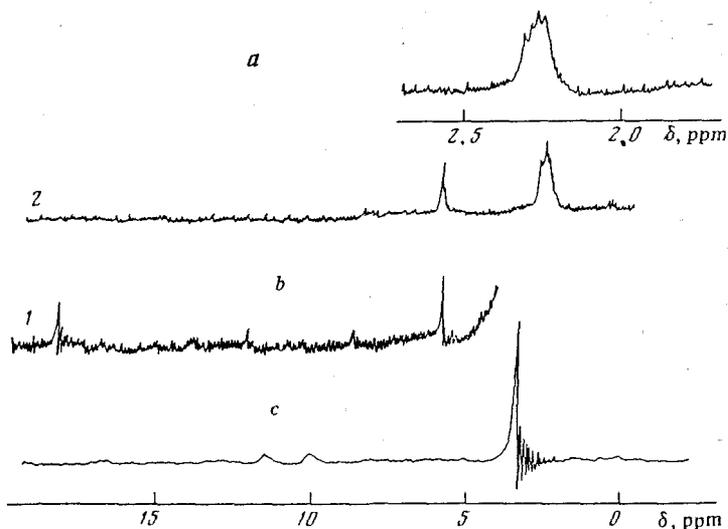


FIGURE 1. Spectra of gaseous mixtures of trimethylamine and trifluoroacetic acid at 200°C . Internal ampoule contains: 1 - CF_3COOH (6×10^{-2} Amagat) and $(\text{CD}_3)_3^{15}\text{N}$ (5 Amagat); 2 - CF_3COOD (5 Amagat) and $(\text{CH}_3)_3^{15}\text{N}$ (2×10^{-2} Amagat).

acid, which was earlier studied in detail by IR spectroscopy in the gas phase, in solutions and in a matrix. Figure 1c, shows the spectrum of a solution of a salt (CF₃COO⁻... H¹⁵N⁺(CH₃)₃) in a mixture of freons at a low temperature [18]. The ion pair present in the solution is characterized by a doublet $\delta = 11.1$ ppm belonging to the group ¹⁵NH⁺ and by a singlet $\delta = 3.15$ ppm due to the methyl groups. Under these conditions a free molecule of trimethylamine exhibits a doublet $\delta = 2.26$ ppm, $J_{\text{NH}} = 3.0 \pm 0.5$ Hz. Thus, in the case of ionization the signal of the methyl group, on the one hand, is shifted down-field for ~ 1 ppm and, on the other hand, becomes converted from the doublet into a singlet. (In the trimethylammonium ion (CH₃)₃¹⁵NH⁺ the spin-spin coupling constant of the methyl protons with the nitrogen nucleus is less than 0.7 Hz and under the conditions of not very high resolution it does not show in the spectra.) Figure 1, a, b depicts the spectra in the gas phase at 200°C (the numerals 1 and 2 denote the samples with excess of the base and acid respectively, which have been described in detail above).

The signal $\delta = 5.9$ ppm is due to the trifluoroacetic acid in the external ampoule; at a high temperature and a very low concentration the acid is entirely in the form of a monomer [15]. The signal $\delta = 18.1$ ppm is due to CF₃COOH (entering into the composition of the complex with a large excess of trimethylamine) in the internal ampoule; the equilibrium (I) in this case is strongly shifted to the right [15]. The trimethylamine signal in the complex is a doublet with $J_{\text{NH}} = 3.0 \pm 0.7$ Hz, shifted for as little as 0.07 ppm, compared with the free-amine signal in the external ampoule. The whole picture is in fair agreement with the conclusion [15] that the adduct of trifluoroacetic acid with trimethylamine in the gas phase is a molecular complex; a ~ 12 ppm shift of the hydroxy group signal in relation to that of the monomer is indicative of a high energy of the hydrogen bond. (It should be noted that the chemical shift of the hydroxyl proton in *molecular* complexes of carboxylic acids with trimethylamine, which was calculated in [22], grows monotonically as the acid strength increases: $\delta = 16.8$ for CH₃COOH, 17.5 for CHCl₂COOH the value of 18.1 ppm for CF₃COOH fits quite snugly into this

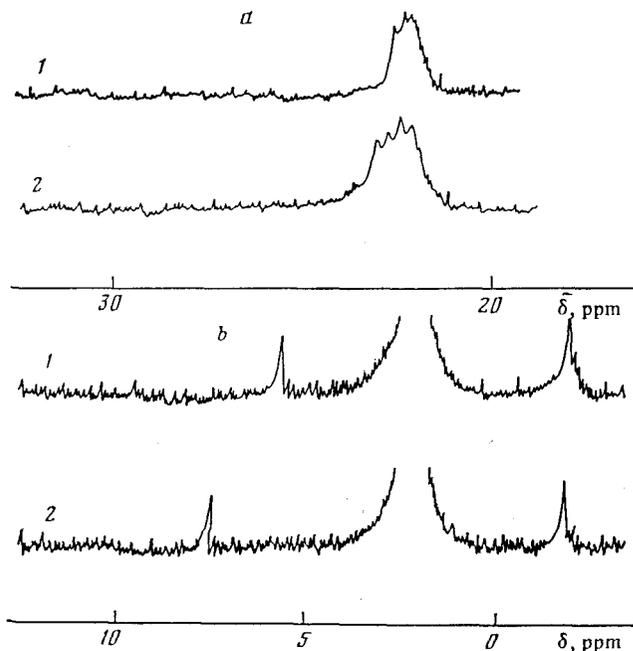


FIGURE 2. Spectra of gaseous mixtures of trimethylamine and hydrogen chloride (deuterium chloride) at 310°C (1) and 270°C (2). Internal ampoule contains: *a* — HCl (40 Amagat) and $(\text{CD}_3)_3^{15}\text{N}$ (2×10^{-2} Amagat); *b* — DCl (4×10^{-2} Amagat); and $(\text{CH}_3)_3^{15}\text{N}$ (40 Amagat).

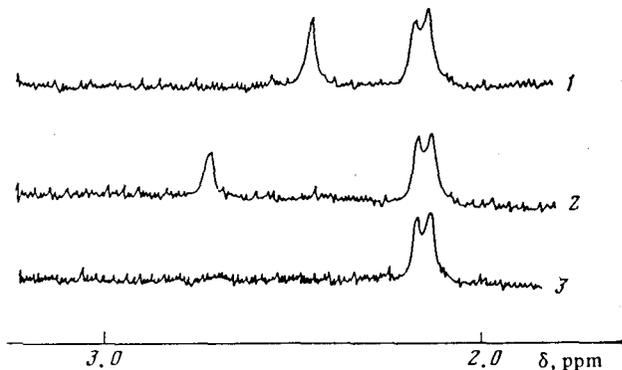


FIGURE 3. Spectra of gaseous mixtures of trimethylamine and hydrogen bromide (deuterium bromide) at 320°C (1), 280°C (2) and 200°C (3). Internal ampoule (2, 3) contains: DBr (40 Amagat) and $(\text{CH}_3)_3^{15}\text{N}$ (2×10^{-2} Amagat); external ampoule (1) contains: $(\text{CH}_3)_3^{15}\text{N}$ (4×10^{-2} Amagat) and argon (20 Amagat).

series. In the condensed medium in the second complex, a partial, and in the third complex, a complete transfer of the proton occurs, accompanied by a sharp increase of the proton shielding, up to 11.1 ppm.)

The spectra of the system trimethylamine - hydrogen chloride (deuterium) are shown in Fig. 2. At a minimum temperature, such that the HCl signal in the internal ampoule can still be observed, as the excess of $(CD_3)_3^{15}N$ increases up to 2500-fold, the chemical shift of this signal tends to the value of 7.5 ± 0.6 ppm, which corresponds to a shift of ~ 10 ppm in relation to the monomer. This value alone reveals nothing about the structure of the complex. The signal of the group CH_3 in this complex, as in the case of CF_3COOH , is a doublet with splitting of ~ 3 Hz, shifted less than for 0.1 ppm in comparison with the doublet of free amine (Fig. 2, a). This means that no amine ionization takes place.

Comparison with the data reported in [18] shows that the complex $(CH_3)_3N \cdot HCl$ in the gas phase bears no resemblance to that possessing a "quasi-symmetrical" hydrogen bond with a "shared proton" [10, 12] either. Indeed, in the symmetrical ion $[(CH_3)_3NHN(CH_3)_3]^+$, in which the presence of such a bond can be suspected, the signal due to the CH_3 groups is shifted 0.4 ppm in relation to the monomer, and the signal of the bridging proton is at 18 ppm [18]. Consequently, the adduct of trimethylamine with hydrogen chloride in the gas phase is a molecular complex with a hydrogen bond. Estimates of the hydrogen bond energy, made by analyzing the dependence of the chemical shift of the observed HCl signal upon the amine concentration and on the temperature (by following the procedure described in [23]), give the value of $\Delta H = 9 \pm 2$ kcal/mol, this being rather at variance with the theoretical value of ~ 20 kcal/mol [6].

Experimental data [24] indicate that solid NH_4Cl can be formed from gaseous H_3N and HCl only in the presence of trace amounts of water. In view of a possibility of proton transfer inside the complex induced by water molecules, we recorded the spectra of gaseous mixtures $(CH_3)_3^{15}N + DCl + D_2O$. But even with the concentration of water ~ 2 Amagat, i.e., in the case of at least a hundredfold excess of water in relation to the complex $(CH_3)_3N \cdot DCl$

present in the mixture, we could find no changes in the chemical shift and the doublet splitting value of the signal due to the methyl groups, as compared with the spectrum presented in Fig. 2, *a*.

Figure 3 shows the spectra of the system $\text{DBr} + (\text{CH}_3)_3^{15}\text{N}$. (Unfortunately, the pressure of the complex vapor being low, we could not identify the signal of HBr contained in the complex with $(\text{CD}_3)_3\text{N}$. The possibility of this signal being masked by the absorption of the remaining protons in the amine cannot be ruled out.) As the DBr concentration increases, the chemical shift of the signal due to the trimethylamine in the internal ampoule tends to 0.8 ± 0.1 ppm in relation to the signal of the monomer; in this case no doublet splitting of the signal is observed, i.e., the spin-spin coupling constant for the methyl protons and ^{15}N nucleus is smaller than 1.5 Hz.

These spectroscopic changes unambiguously point to a proton transfer to the nitrogen atom. The assumption that the equilibrium in bimolecular in character, i.e., that, basically, complexes with a 1:1 composition and free molecules are present in the mixture, is supported by the analysis of the dependence of the chemical shift of the methyl protons on the concentration of deuterium bromide and on the temperature, carried out in conformity with the procedure set forth in [23]. The calculated chemical shift of the methyl protons of the complex is 3.0 ± 0.1 ppm, this value being rather close to the corresponding value for an ion pair in solution [18]. The enthalpy of the complex was found to be equal to $\Delta H = 13.6 \pm 1.5$ kcal/mol, but in this case it bears no direct relationship to the hydrogen bond energy.

Thus, the interaction of trimethylamine with hydrogen chloride in the gas phase leads to the formation of a molecular complex with a hydrogen bond. Since the proton affinity of the ammonia molecule is considerably smaller than that of the trimethylamine molecule [25], the complex $\text{H}_3\text{N} \cdot \text{HCl}$ is doubtlessly unimolecular as well under these conditions, its energy most likely being smaller than 9 kcal/mol as measured for $(\text{CH}_3)_3\text{N} \cdot \text{HCl}$. This is fully in agreement with the results of the nonempirical quantum-chemical calculations [5]. The complex of trimethylamine with hydrogen bromide is close in its structure to the ion pair $\text{A}^- \dots \text{HB}^+$; this is consistent with the

lower proton affinity of the bromide ion compared to the chloride ion [26]. This proves that in principle proton transfer between the uncharged molecules of an acid and a base in the gas phase is possible. We have found no complexes of an intermediate type with a "shared proton"; nevertheless, one cannot rule out the possibility that a complex of trimethylamine with some acid having a strength intermediate between HCl and HBr will feature such a structure. We think it more likely that such complexes are not characteristic of the gas phase (as well as of solutions in nonpolar solvents [17]), and that their formation becomes possible [10, 12] only owing to specific matrix effects.

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