A LOW-TEMPERATURE NMR STUDY OF THE STRUCTURE OF THE IONIC COMPLEXES OF PHOSPHORYL COMPOUNDS WITH A HYDROGEN BOND

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In studying systems with strong hydrogen bonding, a major question concerns the shape of the potential surface and the localization of the proton in the hydrogen bridge [1]. Useful information relative to this question may be obtained by analysis of the coupling constants of the labile OH or NH proton with the other nuclei of the components of the complex [2].

Under ordinary conditions, splitting of the labile proton signal for systems with strong hydrogen bonding is, as a rule, not observed due to rapid exchange processes. However, at temperatures close to liquid nitrogen temperature, these exchange processes are slowed to an extent permitting the observation of separate signals belonging to nonequivalent protons of different complexes with retention of their spin-spin structure [2]. Unfortunately, the linewidth in the NMR spectra under these conditions is several hertz in the optimum case and, thus, only rather strong coupling may be observed. The hydrogen-bonded complexes (H-complexes) of phosphoryl compounds are convenient compounds for these studies since the ^{31}P nucleus has spin $^1/_2$ and a rather high magnetic moment.

In the present work, low-temperature ^1H NMR spectroscopy was used to study two types of complexes in which the phosphoryl group is part of either the acid or basic part of the molecule.

1. Ionic complexes of trifluoromethylsulfonic acid with phosphoryl bases: $(C_8H_{17})_3P=O$ (1), $(C_2H_5)_2PON(C_2H_5)_2$ (2), and the dioxide $(C_2H_5)_2P(O)CH_2CH_2P(O)(C_2H_5)_2$ (3).

2. Complexes of diethylphosphoric acid with dimethylformamide (4), dimethylsulfoxide (5), THF (6), and other ionic complexes of the type $(C_2H_5O_2PO_2)_2^-HX^+$ with a homoconjugated anion, where $X = N(C_4H_9)_4$ or $(CD_3)_3{}^{15}NH$.

A mixture of freons $CDF_2Cl + CDFCl_2$ which freezes at ∿ 90°K was used as the solvent. To eliminate moisture, the phosphoryl bases were maintained for 24 h at 10^{-3} torr at room temperature and then subjected to molecular distillation at 10^{-5} torr. The solution of diethylphosphoric acid in CH_2Cl_2 was dried over P_2O_5. After distillation of the solvent the acid was subjected to molecular distillation at room temperature. A sample of trifluoromethylsulfonic acid was repeatedly distilled at 0.5 torr in a stream of dry argon. The freon mixture was obtained by the fluorination of deuterochloroform (99.7% isotopic purity) by the method of Rappoport and Il'inskaya [3] and purified by vacuum distillation at -60°C over P_2O_5. The ampuls were filled in a drybox in an argon atmosphere. (Traces of moisture in the solution hinders the appearance of spin-spin structure for the labile proton signals even at low temperature). Then, the ampuls were attached to a vacuum system, cooled with liquid nitrogen, evacuated to 0.001 torr, and solvent was distilled in. The ampuls were degassed by the cutoff method and sealed. The spectra were taken on Jeol C-60 HL and Bruker HX 90 spectrometers for concentrations from 0.001 to 0.01 mole/liter.

A thin single line is found in the spectra of pure trifluoromethylsulfonic acid at such low temperatures. The position of this line is virtually independent of temperature from 100 to 160°K (Fig. 1a). Under these conditions, the acid is apparently present in solution as a cyclic dimer. The spectrum of a solution of trioctylphosphine oxide (1) in the presence of excess acid (Fig. 1b) shows, in addition to the dimer signal, a doublet with $\delta = 15.6$ ppm $J^*_{BH^+} = 25 \pm 5$ Hz; this spectrum is not altered by tenfold dilution. The doublet may be assigned to the 1 : 1 acid–base complex and this complex is the $\geqslant POH^+ \ldots {}^-OSO_2CF_3$ ion pair. The spectrum of the ion pair formed upon the protonation of amide (2) has a similar appearance. The spin-spin splitting in this spectrum for the OH proton signal with coupling con-

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*J_{BH^+} and J_{BHB^+} designate J_{PH} in protonated phosphoryl bases.

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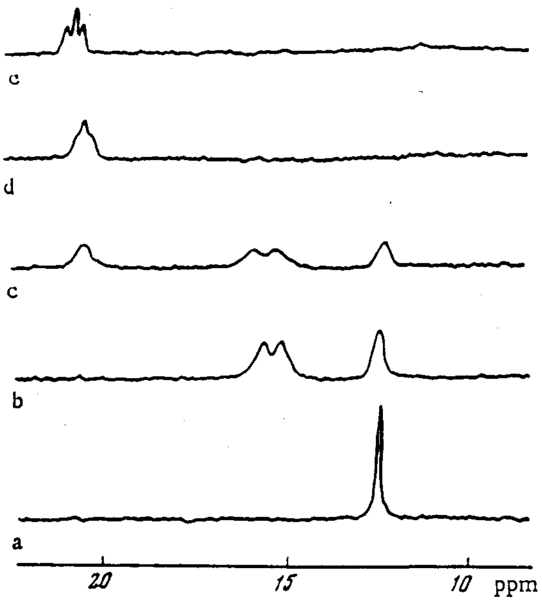


Fig. 1. ^{1}H NMR spectra of solutions containing: CF_3SO_2OH (0.005 mole/liter) (a), CF_3SO_2OH (0.005 mole/liter) and $(C_8H_{17})_3PO$ (0.003 mole/liter) (b), CF_3SO_2OH (0.005 mole/liter) and $(C_8H_{17})_3PO$ (0.005 mole/liter) (c), CF_3SO_2OH (0.003 mole/liter) and $(C_8H_{17})_3PO$ (0.007 mole/liter) (d), and tetraethylethylenediphosphine dioxide (0.006 mole/liter) and CF_3SO_2OH (0.002 mole/liter) (e) in a mixture of freons CDF_2Cl + $CDFCl_2$ at 110°K.

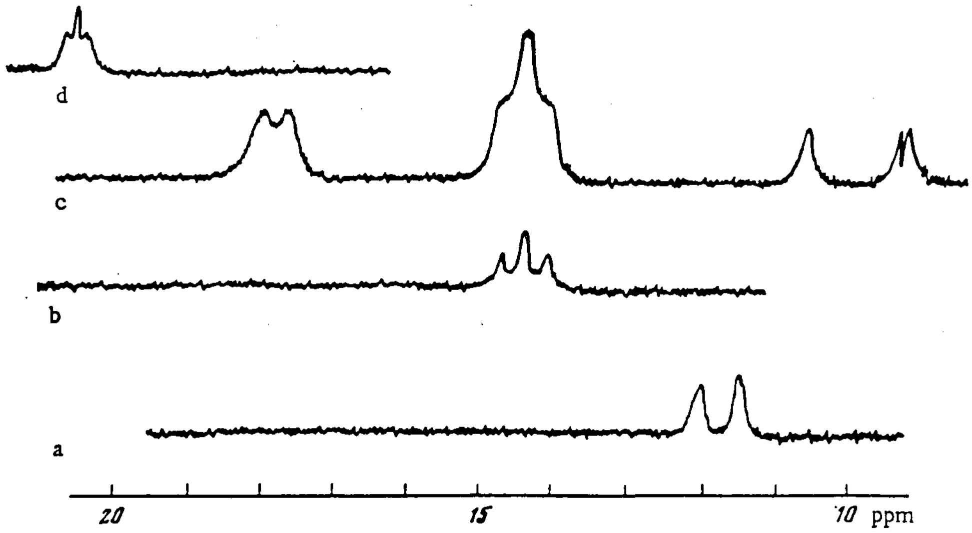


Fig. 2. Spectra of solutions containing: DEP (0.01 mole/liter) and $(CH_3)_2SO$ (0.02 mole/liter) (a), DEP (0.002 mole/liter) (b), DEP (0.03 mole/liter) and $(CD_3)_3{}^{15}N$ (0.01 mole/liter) (c), and the acid salt of DEP with the tetrabutylammonium cation (0.01 mole/liter) (c), and the acid salt of DEP with the tetrabutylammonium cation (0.01 mole/liter) (d). DEP) diethylphosphoric acid.

stant ∿ 20 Hz indicates that the protonation occurs at the oxygen atom and not the nitrogen atom.

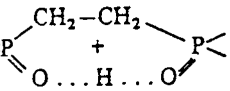
In earlier work [4, 5], we have shown that the titration of phosphoryl bases by strong acids in nitromethane proceeds in two steps and a homoconjugated ion BHB^+ is formed in the first step

$$\begin{aligned} 2B + HA &= BHB^+A^-, \\ BHB^+A^- + HA &= 2(BH^+ \ldots A^-), \end{aligned} \qquad \text{(I)}$$

while the fully protonated structure BH^+ appears only in the case of excess acid. Indeed, upon decreasing the excess of CF_3SO_2OH, the intensity of the ion pair doublet drops (Fig. 1c) and a low-field signal with $\delta = 20.8$ ppm appears. The doublet disappears in the case of excess base (Fig. 1d). In accord with scheme I, the low-field signal may apparently be assigned to the 1 : 2 complex with the BHB^+ ion. Indeed, triplet structure is seen for this signal, indicating that the proton interacts simultaneously with two equivalent phosphorus nuclei.

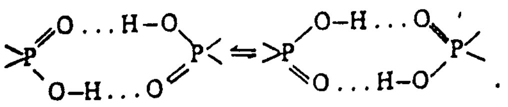
In the symmetrical AHA^- and BHB^+ ions, the proton may be either localized in the central potential minimum or execute a reversible transition in a symmetrical double potential well. In the case of a very high potential barrier, the proton migration proceeds slowly on the NMR time scale and the proton signal will be a doublet with splitting $J_{BHB^+} = J_{BH^+}$ (or ($J_{AHA^-} = J_{AH}$). In the case of rapid migration, as shown in our previous work [2], averaging of the spectra leads to a triplet structure with $J_{BHB^+} = (^1/_2)J_{BH^+}$. The same behavior should be found in the spectra of the cyclic acid dimers in the case of rapid proton exchange within the dimer. Finally, the signal for the proton in a central potential minimum is a triplet with splitting $J_{BHB^+} < J_{BH^+}$, as observed, for example, in the spectrum of the FHF^- ion [6].

In our case, it is rather difficult to find the coupling constant in the $BHB^+ \cdot A^-$ complex since the exchange processes which proceed at a considerable rate even at 100°K leads to line broadening in the spectrum. However, we see that the splitting in the triplet is significantly less than in the doublet of the $BH^+ \ldots A^-$ ion pair. However, the bridge proton signal in the spectrum of a solution containing a slight excess of dioxide (3) and CF_3SO_2OH is a rather well-resolved triplet (Fig. 1e) with $\delta = 21.4$ ppm and $J_{BHB^+} = 6.6 \pm 0.8$ Hz. Unfortunately, we were unable to obtain a spectrum of the fully protonated form of the dioxide; the cyclic homoconjugated cation



apparently has very high stability and is not decomposed by an excess of acid. It would appear, however, that the values for J_{BH^+} to a first approximation, are the same for all phosphine oxides. In this case, $J_{BHB^+} \approx (^1/_4)J_{BH^+}$ and we may conclude that the proton is found in a central potential well (or in a double well, in which the lowest vibrational level lies above the barrier, which is virtually the same experimentally) in homoconjugated BHB^+ ions of phosphoryl compounds. This conclusion is in accord with the x-ray structural data for the crystalline salt, $2(R_3P{=}O) \cdot HClO_4$ [7], in which a very small O—O internuclear distanc- (2.4 Å) was found.

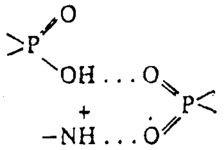
Diethylphosphoric acid gives hydrogen-bonded molecular complexes with oxygen-containing proton acceptors. As an example, Fig. 2a shows the spectrum of this acid with dimethylsulfoxide. The OH signal is a doublet with $J^*_{AH} = 22 \pm 2$ Hz. The same value is found when we take bases (4) or (6) as the acceptor and probably is the same as the coupling constant in the free $(C_2H_5O)_2POOH$ molecule. Figure 2a shows the OH group proton signal in a solution of pure acid (without acceptor) at low concentration, the triplet with $J_{(AH)_2} = 12 \text{ Hz} \approx (^1/_2)J_{AH}$ indicates that the acid is found in solution as a cyclic dimer with rapid proton exchange within the complex:



$^*J_{AH}$ indicates J_{PH} in phosphorus acids.

We note that proton exchange between dimers, which would lead to the disappearance of spin-spin structure, does not occur since the lifetime of the dimer at low temperature is rather long. The OH group proton signal in a solution of the acid salt of diethylphosphoric acid with the almost spherical tetrabutylammonium cation (Fig. 2d) is a triplet although the very low value for $J_{AHA} = 5$ Hz $\approx$ ($^1/_4$)J_{AH} indicates a centered or close-to-centered hydrogen bond in the homoconjugated AHA^- anion.

The anion symmetry may be largely eliminated if the tetraalkylammonium cation, which is incapable of forming a hydrogen bond, is replaced by a trialkylammonium cation. Figure 2c shows the spectrum of a solution containing trimethylamine $(CD_3)_3\ ^{15}N$ (this isotopic modification was used for ease in assignment of the spectral lines) and an excess of diethylphosphoric acid. The spectrum has a triplet with δ = 14.6 ppm of the acid dimer and signals for the 2 : 1 complex, namely,



a doublet of the $^{15}NH^+$ proton at high field indicating complete protonation of the amine, and a downfield doublet with δ = 17.7 ppm with complete J_{AH} = 22 Hz related to the OH group proton in the asymmetrical $AH...A^-...HB^+$ ion. This spectrum shows that the bridge proton in this complex is found near one of the oxygen atoms of the anion. Unfortunately, it is difficult say whether the potential surface has a second minimum corresponding to the less favorable $A^-...HA...HB^+$ form of the complex since even a small difference in energies at such a low temperature should lead to a virtually complete shift in the equilibrium towards the more favorable form.

Thus, analysis of the spin-spin structure of the signal due to the labile proton in complexes with a strong hydrogen bond indicates the location of the proton in the hydrogen bridge. For symmetrical ions such as AHA^- and BHB^+, this permits us to find the qualitative form of the potential energy surface (with one or two minima).

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