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STRUCTURE OF MOLECULAR AND IONIC H-BONDED COMPLEXES OF HEXAMETHYLPHOSPHORTRIAMIDE BY LOW TEMPERATURE NMR IN FREON SOLUTION

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ABSTRACT

The ^{1}H NMR spectra have been obtained for a number of H-bonded complexes formed by the interaction of OH-acids of increasing strength and $[(CH_3)_2N]_3PO$ (HMPT) in a freon mixture (CDF_2Cl + $CDFCl_2$) at 100 K. The signals of the complexes with moderately strong acids ($pK_a > -2$) are singlets, which proves that they have a molecular structure, AH...B. With stronger acids, a doublet spin-spin coupling of the bridge proton with ^{31}P nucleus occurs (J_{PH}=cca 20 Cps) indicating a complete proton transfer, $A^-...HB^+$. The conclusion has been drawn that a sharp change in structure is caused by gradual change in the interaction energy as measured by ΔpK_a. The spectra of a number of conjugated complexes, $[BHB']A^-$, have been taken. If B=B', the homoconjugated cation with a centrosymmetric H-bond is formed, followed by a strong decrease in J_{PH}.

INTRODUCTION

The interaction between a protic acid, AH, and a neutral base, B, in aprotic low-polar solvents results in the formation of a hydrogen-bonded complex. Its structure, depending upon the acid-base strength of the partners and solvent polarity, is known to vary from molecular, AH...B, to ionic, $A^-...HB^+$ [1]. The proton affinity difference, $\Delta PA=PA(B)-PA(A^-)$, where $PA(A^-)$ is the proton affinity of an anion in a gaseous phase as well as a more available value, $\Delta pK_a=pK_a(BH^+)-pK_a(AH)$, are usually taken as values roughly characterizing the energy of the acid-base interaction [1-3]. The question of how a molecular complex is gradually transformed into an ionic pair as ΔpK_a is varied continuously is of particular interest. In [3], the IR absorption spectra of a number of H-bonded complexes of HCl and HBr isolated in a nitrogen matrix were obtained. The value of the frequency of the stretching proton vibration in an H-bridge, ν_s,appeared to depend systematically,though not monotonically,upon the proton affinity difference,ΔPA.On this basis, the gradual change in structure of the complexes was concluded.The minimal vibrational frequency was considered by the authors to correspond to a "completely shared proton",the heteronuclear counterpart of centrosymmetric H-bonds such as those in HF_2^- and HCl_2^-.Subsequently,the varieties of the complexes of OH-acids with amines [4,5] and pyridine [6];HCl and HBr with O-bases [7];the OH...O -type complexes [8,9] and some charged complexes of the formiate-ion,$HCOO^-$,with carboxylic acids [IO],were studied.All spectroscopic values indicating the strength of an H-bond (such as the frequency and integral intensity of the stretching vibration, ν_s,and the chemical shift of a bridge proton),plotted against ΔpK_a,were shown to pass through their extrema.However,these spectroscopic values cannot be taken as a characteristics of "the degree of proton transfer".Thus,such relationships do not represent an unambiguous proof of the gradual ionization of a molecular complex upon an increase in the interaction energy,and an extremal point in the plot can correspond to no "quasisymmetrical" complex.In a great number of papers [II-I8] the existence of the "molecular-ionic tautomerism"of H-bonded complexes was proved:

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

which is largely characteristic of the OH...N H-bonds.As the acid-base interaction gets stronger,the equilibrium (I) is shifted to the right.The tautomerism implies a sharp change in structure;and at low temperature,when the equilibrium (I) must be shifted strongly to a more profitable (in terms of energy) isomer,one would observe either a molecular or ionic complex,depending on the ΔpK_a value.It is difficult to say how widespread is the molecular-ionic tautomerism;as far as we know in the case of uncharged OH...O H-bonded complexes the equilibrium (I) has never been reported.

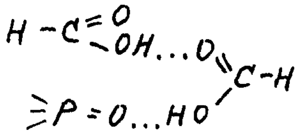
In the present work some complexes of a strong O-base, $[(CH_3)_2N]_3PO$ (HMPT), with a range of strong OH-acids have been studied by means of ^{I}H NMR at low temperature in a freon mixture,$CDF_2Cl+CDFCl_2$. As shown in [IO,I9,20],at a temperature of about IOO K,the signals of OH-protons belonging to various complexes in equilibrium can be observed separately,their spin-spin coupling being discernible.The spin-spin coupling value of a bridge proton with the ^{3I}P nucleus of HMPT has been used as a parameter characterizing "the degree of proton transfer".For a completely protonated HMPT molecule this value was measured as 22±I Cps [20].

EXPERIMENTAL

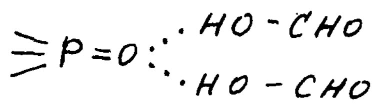
The bases used,HMPT,dimethylsulphoxide(DMS),dimethylacetamide (DMA),were dried by zeolytes and afterwards distilled in dry argon flow at low pressure.HMPT was, in addition, exposed to high vacuum molecular distillation at $30^{\circ}C$.The extremely hygroscopic trimethylaminoxide and trimethylphosphinoxide were heated for several days at $+64^{\circ}C$;IO^{-4} Torr,to remove water.Carboxylic acids were purified by conventional methods followed by repeated vacuum sublimation at low temperature.The anhydrous $HClO_4$ was used immediately upon distillation together with an excess of H_2SO_4.The mixture of freons,CDF_2Cl+CDF_2Cl (4:I),was used as a solvent;the freon was redistillated at $-70^{\circ}C$ through a layer of zeolytes.The technique of obtaining samples suitable for the low temperature NMR in liquified gases was reported in [20].The spectra were recorded by a JEOL C-60 HL spectrometer.

RESULTS AND DISCUSSION

The spectra of the complexes of HMPT with formic acid were given in the previous paper (see Fig.I in [I9]).In an excess of the base,the only singlet,δ=I4.6 ppm,was observed belonging to the molecular I:I complex.In an excess of the acid, two more singlets of equal intensity, δ=I5.2 and I3.8 ppm,appear and are attributed to the 2:1 complex



Similar are the spectra of solutions,containing HMPT and dichloroacetic,$CHCl_2COOH$; the chemical shifts of the complexes formed are listed in Table 1.(There is some ambiguity in attributing the observed signals having equal intensities to the two OH-protons of the 2:I complex.It is clear,however,that polarization caused by the addition of the second acid molecule will lead to some strengthening of the H-bond OH...O=P.Thus,it seems natural to attribute the low-field signal (δ=I5.2 ppm in the case of HCOOH) to the OH...O=P proton in the 2:I complex.It is to be noted that in a complex formed by two lone pairs of the P=O oxygen atom



these two OH-protons would be equivalent.).

The spectra of solutions containing HMPT and trifluoroacetic acid,CF_3COOH,are shown in Fig.1.An excess of the base taken,a narrow singlet,δ=I8.6 ppm,is observed, which must be attributed to the I:I complex of pure molecular structure.On addition of some excess of CF_3COOH,a singlet,δ=I5.6ppm,and a doublet,δ=I6.7 ppm,appear

TABLE I.Chemical shifts and spin-spin coupling values of the bridge proton in the complexes of HMPT with some OH-acids (IOO K,Freon mixture).

Acid	pK_a *	δ (ppm)	J_{PH} (Cps)
HCOOH	3.74	I4.6	$<$I
$(HCOOH)_2$	-	I5.2	- " -
$CHCl_2COOH$	I.25	I6.8	- " -
$(CHCl_2COOH)_2$	-	I7.3	- " -
CF_3COOH	0.23	I8.6	- " -
HNO_3	-I.64	I7.2	- " -
$(CF_3COOH)_2$	-	I6.7	20 ± 2
CH_3SO_2OH	-3	I5.4	20 ± 2
CF_3SO_2OH	-8	I4.0	22 ± 2
$HClO_4$	-8	I3.4	22 ± 2

* G.Kortum,W.Vogel,K.Andrussow,Dissociation constants of organic acids in aqueous solution,Plenum Press,N.-Y.,I96I.

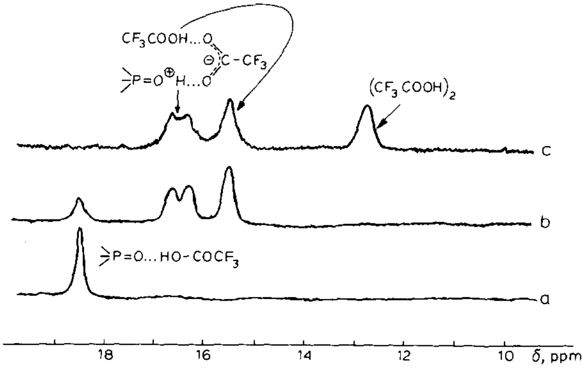


FIG.I. The ^{I}H spectra of solutions,containing CF_3COOH and HMPT at the concentrations: a) $2\cdot IO^{-3}$ and $5\cdot IO^{-3}$mole/L; b) $3\cdot IO^{-3}$ and $2\cdot IO^{-3}$mole/L; c) $6\cdot IO^{-3}$ and $2\cdot IO^{-3}$ mole/L, in the freon mixture at IOO K.

together.With a change in concentration of the acid,only the relative intensities of the signals are altered,their chemical shifts being unaffected.This implies that exchange processes are slow enough and all the signals are not averaged.As the δ=I6.7 ppm doublet coalesces on RF saturation at ^{3I}P frequency,its splitting must be caused by spin-spin coupling with the ^{3I}P nucleus.The value of J_{PH}=20±2 Cps proves beyond all shadow of doubt that a complete proton transfer occured in the complex,which must be considered as an ionic pair.Thus,addition of a second acid molecule to the complex results in a qualitative change of the type of H-bonding.Earlier a similar effect was reported for the complexes of acetic acid with triethylamine [2I].

Finally,for the complex of a stronger acid,CH_3SO_2OH,even the signal of the I:I complex is a doublet,J_{PH}=22±2 Cps,which indicates a complete proton transfer. Fig. shows the spectra of HMPT and one of the strongest uncharged acids known, CF_3SO_2OH.In an excess of the acid (Fig.2,a),a singlet δ=I0.9 ppm can be observed together with a doublet δ=I4.0 ppm, J=22±2 Cps.The δ=I0.9 ppm signal is seen in the absence of a base;it belongs,most likely,to the dimer of CF_3SO_2OH.When the excess of the acid decreases down to the equimolecular ratio,this singlet disappears.At the same time the doublet of the I:I ionic pair diminishes.(Our attempts to register some signals which could be attributed to the 2:I complex with two CF_3SO_2OH molecules have failed).Instead of the doublet,a triplet, δ=20.6 ppm,J_{PH}= =6±I Cps,appears (Fig.2,b).Taken into account the considerations reported in

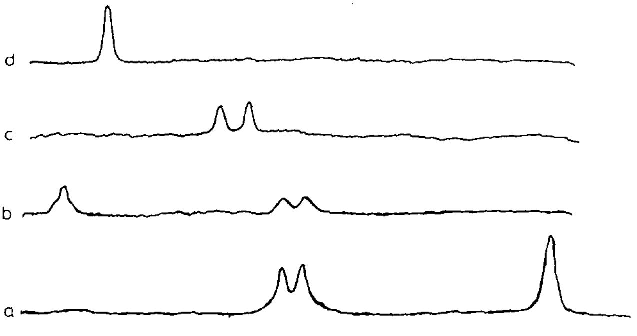


FIG.2. The ^{I}H spectra of solutions in the freonmixture at I00 K,containing HMPT ($4\cdot I0^{-3}$ mole/L) and : a) CF_3SO_2OH ($I0^{-2}$ mole/L); b) CF_3SO_2OH ($2\cdot I0^{-3}$ mole/L); c) CF_3SO_2OH ($4\cdot I0^{-3}$ mole/L) and $(CH_2)_4O$ ($I0^{-2}$ mole/L); d) CF_3SO_2OH ($4\cdot I0^{-3}$ mole/L) and $(CH_3)_3NO$ ($I0^{-2}$mole/L).

[I9,20],the triplet may be identified as corresponding to a homoconjugated $[B...H...B]^+$ cation involved in an ionic pair with the $CF_3SO_3^-$ anion.A strong decrease in spin-spin coupling value of a bridge proton is typical of centrosymmetrical H-bonds,where the proton is not preferentially associated with any B fragment [I9].In an excess of the base,the spectrum consists only of the triplet which points to its high stability.

On the addition of another base such as THF,DMS or DMA to the solution containing equimolecular amounts of HMPT and CF_3SO_2OH,a doublet arises (Fig.2,c) shifted to a higher field compare to the doublet of the I:I ionic pair.The doublet can be attributed to a heteroconjugated cation,$BH^+...B'$,involved in an ionic pair. Here,the spin-spin coupling value,J_{PH},is close to the full value,22 Cps;this implies the bridge proton localized in the potential well near the O-atom of a PO group.An increase in the strength of a base B'involves a sharp decrease of J_{PH}; in the $[BHB']^+$ cation this value is less than I Cps,and no splitting of the corresponding signal is observed.Thus,in this complex,the proton is best considered to be attached to the O-atom of the N→O group.

A concerted consideration of a variety of the data listed in Tables I, can display the systematics of proton transfer in the hydrogen bonds as a function of ΔpK_a.The chemical shifts of the bridge proton,in neutral (AHB) and charged $(BHB')^+$ complexes,vary in a large range which can be an indication of a large difference in H-bonding energy values.The δ value plotted against ΔpK_a passes through a maximum,which is in accordance the data reffered to above [3-IO].In the

TABLE 2.Chemical shifts and spin-spin coupling values of the bridge proton in some conjugated ions of the protonated HMPT, $[B...H...B']^+ \cdot CF_3SO_3^-$ (IOO K).

Base	(ppm)	J_{PH} (Cps)
$(CH_2)_4O$	I7.2	22 ± 2
$(CH_3)_2SO$	I8.9	- " -
$(CH_3)_2NCHO$	I9.7	I9 ± 2
$(CH_3)_3PO$	20.2	I3 ± 5
$[(CH_3)_2N]_3PO$	20.6	6 ± I
$(CH_3)_3NO$	I9.7	< I

case of charged complexes,the maximum corresponds to a centrosymmetrical H-bond with a "completely shared" proton.However,this is not valid for uncharged systems (AHB),where the transformation of a molecular complex into an ionic pair occurs in a very narrow range of ΔpK_a.(Of course,this conclusion is based on the J_{PH} value taken as a quantitative measure of the "degree of proton transfer").Thus, from this point of view the complex of HMPT with HNO_3 must be qualified as a typical molecular complex in accordance with IR evidences [8],and that with CH_3SO_2OH as a typical ionic pair.The maximum in the plot corresponding to a molecular complex $CF_3COOH \cdot HMPT$ merely means the strongest H-bond in the range of complexes studied.It is not impossible,of course,that there exists a complex of HMPT with some acid (e.g.,weaker than CH_3SO_2OH and stronger than HNO_3) where the proton is not attached preferentially to an acid or a base involved,and characterized by an intermediate value of J_{PH}.

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