Journal of Molecular Structure, 75 (1981) 333—337
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

Short communication

PROTON SPIN—SPIN COUPLING IN COMPLEXES OF FORMIC ACID WITH PROTON ACCEPTORS

N. S. GOLUBEV, G. S. DENISOV and A. I. KOLTSOV
Institute of Physics, Leningrad State University, Leningrad (U.S.S.R.)

(Received 19 February 1981)

This article is devoted to a study of complex formation upon interaction between an acid and a base in inert media (such as CCl_4, cyclohexane and freons). It is known that interaction between weak partners AH and B leads to the formation of a complex with hydrogen bonding $AH\cdots B$ whereas reaction between very strong partners results in an ionic complex with hydrogen bonding $A^-\cdots HB^+$, the complex formation involving proton transfer. The most interesting region is that of intermediate interaction energy where the largest spectroscopic effects caused by strong hydrogen bonding have been observed. Two types of complex formation with increase of interaction energy are possible:

1. Molecular—ionic tautomerism which involves reversible proton transfer inside a complex

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

The stronger an acid (or base), the more equilibrium (1) is shifted to the right [1, 2].

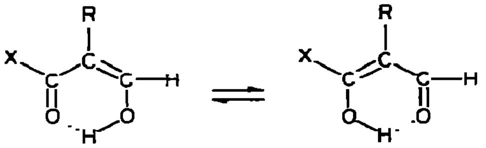
2. The gradual change in structure of a complex from molecular to ionic, as an acid (or base) gets stronger. This change includes, in particular, the gradual increase of the A—H, and the decrease of the B—H equilibrium distance. The complex is formed in the intermediate region where the proton is not chiefly bound to either fragment A or B (the so called "quasisymmetrical hydrogen bond"). In the case of the same fragments, i.e. A = B, this is a complex with a symmetrical hydrogen bond such as that found in the $[F\cdots H\cdots F]^-$ion. These processes are also applicable in the case of charged acids or bases.

The method of complex formation in a particular acid—base range is usually determined from a set of indirect experimental data, e.g., isotope effects in vibrational and NMR spectra [3—5]. We believe that more direct information might be obtained from spin—spin coupling between the proton forming the hydrogen bond and some nuclei belonging to A and B fragments.

In the case of the tautomerism $AH\cdots B \rightleftharpoons A^-\cdots HB^+$, when the equilibrium shifts to the right (which may be achieved by temperature change), the effective value of the splitting caused by the interaction of the proton with the A nucleus is bound to decrease from the J_{AH} value (characteristic of the

0022—2860/81/0000—0000/$02.50

pure AH···B structure) down to zero, as the interaction through a hydrogen bond is very weak. The analogous value for the B fragment must increase from zero up to J_{BH}. The chemical shifts of the H, A and B nuclei must also be strongly influenced by the temperature change. This is the picture observed in the NMR spectra of the systems with intramolecular proton transfer [6]



(2)

and also in the tautomeric complexes of carboxylic acids and trimethylamine in CHF_2Cl [7]. The proton signal of the AH···A system with proton migration must be the triplet with effective coupling value $\frac{1}{2} J_{AH}$. Indeed, such a value was found in the formally symmetrical system (eqn. (2)) where X = H [8].

In the case of quasisymmetrical hydrogen bonding the spectra will not be affected greatly by temperature, as there is no equilibrium in the complex to be shifted. At the same time the spin—spin coupling values will differ from J_{AH} and J_{BH}. In complexes with a symmetrical hydrogen bond, the splitting observed will be considerably less than $\frac{1}{2} J_{AH}$. Indeed, the picture described above has been found in the spectra of $[F \cdots H \cdots Hal]^-$ ions (Hal = F, Cl, Br) [9].

The aim of the present work is to find the method of complex formation in a range of HCOOH complexes with the oxygen bases, using proton spin—spin coupling values. Spin—spin coupling of any nucleus with the carboxylic proton has never been observed because of fast intermolecular proton exchange. However, in refs. 10 and 11 it was shown that in NMR spectra of solutions containing carboxylic acids and proton acceptors, the signals of various complexes could be observed separately at temperatures below 140 K, the proton exchange having no influence on line shapes. In this work, the spectra of HCOOH and mixtures of it with some proton acceptors (tetrahydrofuran (THF), hexamethylphosphortriamide (HMPT) and various tetrabutylammonium carboxylates $RCOO^-NBu_4^+$) have been obtained in $CHClF_2$ at 110—150 K.

EXPERIMENTAL

Formic acid was purified by the conventional method followed by repeated vacuum sublimation at —30°C. HMPT was dried with 13X zeolite, distilled at 90°C and then exposed to molecular distillation at 30°C. The salts were dried under high vacuum for several hours. $CHClF_2$ solvent was purified by low temperature fractional distillation and dried with 3A zeolite in gaseous phase.

The glass tubes in which solutions were prepared were previously evacuated at 300°C to remove molecules adsorbed on the surface. All the operations to prepare solutions were carried out in a glass vacuum unit. The spectra were recorded by a JEOL C-60 HL spectrometer.

RESULTS AND DISCUSSION

In the spectra of solutions containing 0.02—0.05 mol l^{-1} HCOOH and 5—8 fold excess of THF or HMPT at 110—150 K, two well resolved doublets with the same splitting values (11.6 cycles) were observed. As one of these doublets coalesced on RF saturation of the other, the splitting must be caused by spin—spin coupling. The high value of *J* confirmed the non-symmetrical structure AH···B.

In the spectra of HCOOH solutions (0.01—0.02 mol l^{-1}) without any proton acceptor in $CHClF_2$ at 120 K, splitting of the OH signal occurred only when both acid and solvent had been thoroughly purified. The signal was a triplet, the effective coupling value being 5.9 cycles, or $\frac{1}{2}J$ for the complexes with THF and HMPT (Fig. 1), so proving that the signal belonged to the cyclic dimer with a fast migration of protons. As the triplet was not broadened at 120 K, the frequency of this migration at this temperature must be more than 100 cycles s^{-1}. Indeed, in some theoretical papers it has been shown that proton transfer in cyclic dimers may be accomplished by tunneling, and consequently may be fast at any temperature (see, for example ref. 12). The process which causes the coalescence of the triplet at 130 K must be a proton exchange between the dimers. Proton lifetimes determined by this process were 10^{-1}—10^{-2} s at 130—140 K. The lifetime of a dimer limited by hydrogen bond breaking was found to be of the same order [10]. Therefore, proton exchange between the cyclic dimers of formic acid may be supposed as involving in successive stages, the dissociation of one dimer, formation of another and fast proton transfer, the dissociation being the stage which limits the observed rate.

The spectra of complexes of HCOOH with ionic bases $RCOO^-NBu_4^+$ were obtained with 4—5 fold excess of a base. (The same complexes could

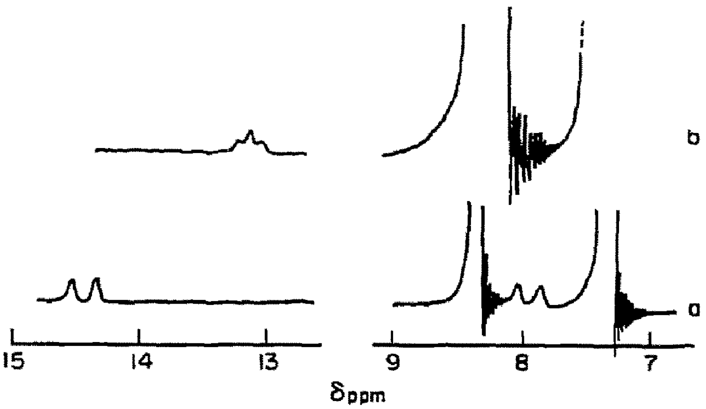


Fig. 1. The ^1H NMR spectra (60 MHz) of solutions containing (a) HCOOH (0.02 mol l^{-1}) and $[(CH_3)_2N]_3PO$ (0.15 mol l^{-1}), and (b) HCOOH (0.01 mol l^{-1}) in $CHClF_2$ at 120 K.

TABLE 1

Chemical shifts and effective spin—spin coupling values of the signal of the bridge proton in some complexes of formic acid with proton acceptors (CHF_2Cl solutions, 120 K)

Acceptor	δ (ppm)	Δ (cycles)
$(CH_2)_4O$	10.2 ± 0.1	11.6 ± 0.3
HCOOH	13.1	11.8 ($\frac{1}{2}$)
$[(CH_3)_2N]_3PO$	14.5	11.6
CF_3COO^-	17.2	10.5
$CHCl_2COO^-$	18.9	7.2
CH_2ClOO^-	19.6	3.5
$HCOO^-$	20.2	<1
CH_3COO^-	18.5	<1
$(CH_3)_3CCOO^-$	17.3	<1

be obtained by the interaction of carboxylic acids RCOOH with the $HCOO^-R'_4N^+$ salt.) In Table 1 the values of the chemical shift and the doublet splitting decrease with increase of the anion basicity. In the symmetrical $(HCOO)_2H^-$ ion no coupling may be observed because it is less than 1 cycle and it does not occur with further strengthening of a base. At the same time deshielding of the OH proton increases, attains its highest value in the symmetrical complex and then decreases. The chemical shifts do not in practice depend on temperature, which proves that there is no tautomeric proton transfer in these complexes. With increase of basicity, the structure of the complex is changed continuously, so that, while the complex of HCOOH with the CF_3COO^- ion could be described as $HCOOH\cdots OCOCF_3^-$, for the complex of HCOOH with the $(CH_3)_3CCOO^-$ ion the structure $HCOO^-\cdots HOCOC(CH_3)_3$ appeared to be more feasible. The complex with the $HCOO^-$ ion is certain to have the symmetrical $HCO\cdots H\cdots OCHO$ hydrogen bond, which agrees with earlier experimental data. Indeed, in the alternative case of the tautomeric complex, the spin—spin coupling value should be close to 5.8 cycles ($\frac{1}{2}J$), as in the cyclic dimer.

CONCLUSIONS

Spin—spin coupling values obtained from NMR spectra at low temperature (100—150 K) have allowed us to establish mechanisms of complex formation in solution which would otherwise be difficult to determine.

REFERENCES

1 G. S. Denisov and V. M. Schreiber, Dokl. Akad. Nauk SSSR, 215 (1974) 627.
2 G. S. Denisov, N. S. Golubev and V. M. Schreiber, Studia Biophysica, 57 (1976) 25.
3 A. Novak, Struct. Bonding (Berlin), 18 (1974) 177.
4 N. N. Schapet'ko, Yu. S. Bogatchev, I. L. Radushnova and D. N. Shigorin, Dokl. Akad. Nauk SSSR, 231 (1976) 404.
5 G. Gunnarson, H. Wennerström, W. Egan and S. Forsen, Chem. Phys. Lett., 38 (1976) 96.

6 R. S. Noy, V. A. Gindin, B. A. Ershov, A. I. Koltsov and V. A. Zubkov, Org. Magn. Reson., 7 (1975) 109.
7 N. S. Golubev, G. S. Denisov and A. I. Koltsov, Dokl. Akad. Nauk SSSR, 232 (1977) 841.
8 R. S. Noy, B. A. Ershov and A. I. Koltsov, Zh. Org. Khim., 11 (1975) 1778.
9 F. J. Fujiwara and J. S. Martin, J. Am. Chem. Soc., 96 (1975) 7625.
10 N. S. Golubev and G. S. Denisov, React. Kin. Catal. Lett., 4 (1976) 87.
11 N. S. Golubev, React. Kin. Catal. Lett., 7 (1977) 225.
12 W. A. Sokalski, H. Romanowski and A. Jaworski, Proc. IIIrd Int. Symp. Specific Interactions between Molecules or Ions, Poland, 1976, p. 507.