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MECHANISM OF PROTON TRANSFER FROM 2-NITROHEXAFLUOROPROPANE TO AMINES

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According to the analysis of NMR kinetic data, the proton transfer from the CH-acid 2-nitrohexafluoropropane to trioctylamine occurs in a hydrogen-bonded complex. The value of the k_H/k_D ratio ($\ngtr 6$) and the linearity of the ln k vs. T^{-1} dependence indicate a classical mechanism of the process.

Исследована кинетика перехода протона от 2-нитрогексафторпропана к аминам. Доказано одновременное присутствие молекулярной и ионной форм в системе. Анализ кинетических данных показал, что переход осуществляется внутри молекулярного комплекса. Величина кинетического изотопного эффекта $k_H/k_D \ngtr 6$ говорит в пользу классического механизма перехода протона.

As a rule, the rate of proton transfer from CH-acids to bases is much lower than in the case of common OH-acids. It is assumed /1/ that proton transfer always occurs through the intermediate formation of a hydrogen-bonded complex. In the case of OH-acids the intermediate complex can be identified spectroscopically /2/. CH-acids are known as extremely weak proton donors in hydrogen bonding, therefore, complex formation in the proton transfer reaction is not evident. As is shown in Refs. /3, 4/, proton transfer from 1,1-dinitroethane (DNE) to amines occurs in a complex with a very weak CH ... N hydrogen bond. We have studied the kinetics of proton transfer from a CH-acid with an acidity close to that of DNE, but with an enhanced ability to form a much stronger hydrogen bond. The pK_a values of DNE and 2-nitrohexafluoropropane $(CF_3)_2CHNO_2$ (NHFP) are equal to 5.2 and 5.0, respectively, whereas their hydrogen bond energies with $(CD_3)_2SO$ in CCl_4 are 2.2 and 4.9 kcal/mol /3/, respectively. The ^{1}H-NMR and ^{19}F-NMR spectra of solutions containing NHFP and trioctylamine (TOA) in $CDCl_3$ in the temperature range from –60 to +60°C were recorded on a TESLA instrument (80 MHz). HMDS and CF_3COOH solutions were used as external standards.

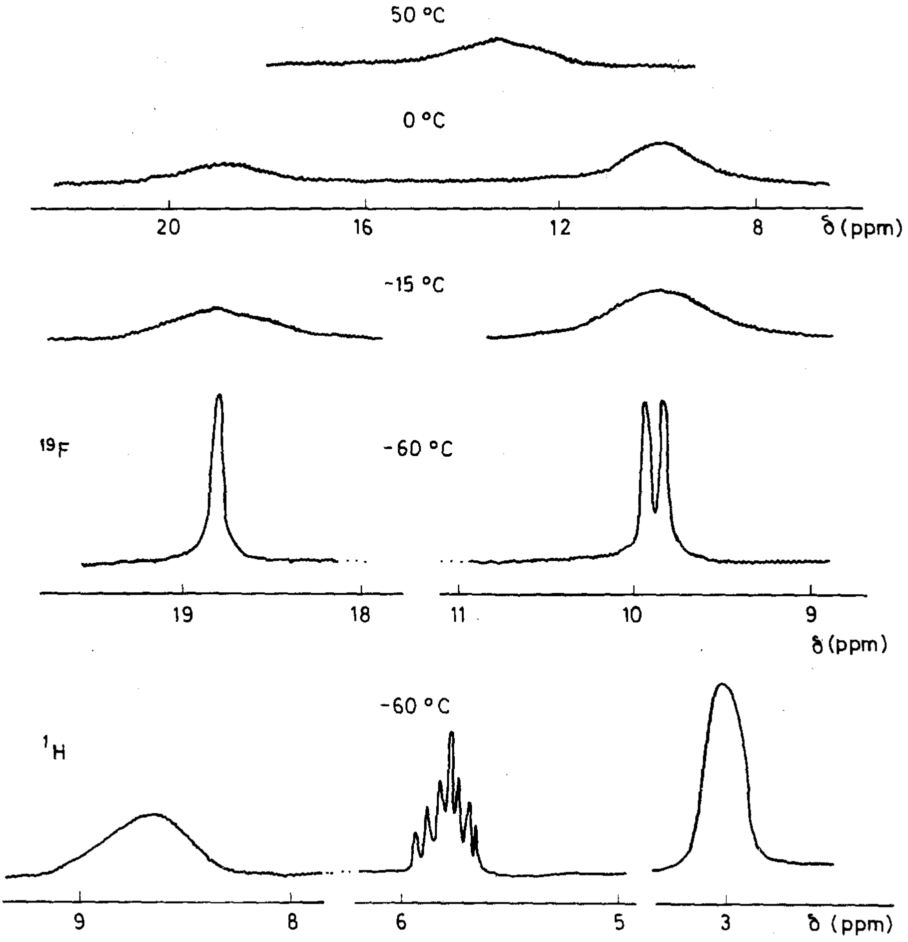

Fig. 1. ^{1}H-NMR and ^{19}F-NMR spectra of a solution containing 0.05 mol/l NHFP and 0.03 mol/l TOA in $CDCl_3$

Spectra of the solutions, containing 0.05 mol/l NHFP and 0.03 mol/l TOA, are illustrated in Fig. 1. The ^{1}H spectrum exhibits a shift of the CH group septet towards lower fields as compared with the free NHFP signal, whose value depends on the reactant concentrations and the temperature (0.3–0.9 ppm). The spectrum also exhibits a wide singlet belonging to the NH^+ proton of the ion pair $[(CF_3)_2CNO_2]^-$ $H[NOct_3]^+$. In the ^{19}F spectrum, besides a $\delta = 9.66$ doublet of the molecular forms, a $\delta = 18.78$ singlet is observed, belonging to the CF_3 group of the ion pair and coinciding with the signal of the tetrabutylammonium salt of NHFP. With increasing temperature, the signal intensity of the ion pair decreases, whereas that of the molecular forms increases. Simultaneously, the signals broaden and the coalescence of the CF_3 doublet and singlet are observed in the temperature range from +10° to 20°C, depending on the concentration. The shape of the signals is determined by the rate of proton transfer from NHFP to the amine. Thus, in the solution the free molecules of acid and base and the hydrogen-bonded complexes and the ion pairs are in equilibrium. Strictly speaking, the presence of molecular complexes cannot be regarded as proof of the proton transfer occurring through their formation. Its mechanism can be clarified only on the basis of the kinetics. For a two-step reaction:

$$K_1 = \frac{[AH \ldots B]}{[AH]\ [B]} = \frac{P}{(1-P)\left[[B]_o - [AH]_o (P+R)/(1+P)\right]}$$

$$K_2 = \frac{[A^- \ldots HB^+]}{[AH \ldots B]} = -\frac{P}{R}$$

$$P = \frac{[AH \ldots B]}{[AH]_o - [A^- \ldots HB^+]} = \frac{\delta - \delta_o}{\delta_c - \delta_o}$$

where P is the concentration ratio of the complex and the total molecular forms, determined from the chemical shifts of the CH-proton multiplet; R is the concentration ratio of the ion pair and the molecular forms determined from the full line shape analysis of the CF_3 signals together with the lifetimes of the mulecular forms τ_m and the ion pair τ_i. Monomolecular rate constants of proton transfer inside the complex are: $k = \tau^{-1}_{AH \ldots B}$; $k_{-1} = \tau_{A^- \ldots HB^+}$. The lifetimes of the equilibrium states are proportional to their relative concentrations, therefore, $\tau_{AH \ldots B} = \tau_m P$. The independence of $k = \tau^{-1}{}_m P^{-1}$ of the concentration may be considered as a criterion for the validity of the mechanism suggested.

Quantitative characteristics of the process were obtained at temperatures from −60 to −10 °C. According to Ref. /3/, the values K_1 and δ_c at the above temperatures were varied by the computer till best coincidence between the experimental and the theoretical dependences of δ on $[AH]_o$ and $[B]_o$ was obtained. Afterwards we determined the values of P and K_2 depending on the temperature and then the values of ΔH_1 and ΔH_2 of processes I and II (6.1 ± 0.6 and 12.4 ± 0.8 kcal/mol, respectively and for DNE 3.0 and 12.0 kcal/mol). Lifetimes of the molecular forms at several concentrations (−30 °C), chemical shifts of the CH-proton at the same concentrations and the $\tau^{-1}_m P^{-1}$ values are listed in Table 1. It can be seen that des-

Table 1

Lifetimes of the molecular forms and monomolecular rate constants of proton transfer in the $(CF_3)_2CHNO_2$-TOA complex in $CDCl_3$ (−30 °C)

$[AH]_0$ (mol/l)	$[B]_0$ (mol/l)	τ_m (sec)	$\delta - \delta_0$ (ppm)	k (sec^{-1})
0.2	0.05	0.0082 ± 0.0005	0.07	$(5.4 \pm 0.5) \cdot 10^3$
0.1	0.04	0.0031 ± 0.0005	0.20	$(5.5 \pm 0.5) \cdot 10^3$
0.05	0.04	0.0012 ± 0.0003	0.45	$(5.9 \pm 0.5) \cdot 10^3$
0.03	0.04	0.0007 ± 0.0001	0.77	$(6.1 \pm 0.5) \cdot 10^3$

($\delta_0 = 5.46$ ppm, $\delta_c = 8.7$ ppm)

Table 2

Kinetic characteristics of proton and deuteron transfer in molecular complexes

Acid	$k^{283}_{(H)}$ (sec^{-1})	$k^{283}_{(D)}$ (sec^{-1})	$E_{(H)}$ (kcal/mol)	$E_{(D)}$	lg $A_{(H)}$	lg $A_{(D)}$
$(CF_3)_2CHNO_2$	$(2.1 \pm 0.5) \cdot 10^4$	$(3.6 \pm 0.3) \cdot 10^3$	4.7 ± 0.5	5.5 ± 0.5	7.9	7.7
$CH_3CH(NO_2)_2$	8.2 ± 0.8	2.7 ± 0.4	7.9 ± 0.6	8.4 ± 0.6	7.0	6.8

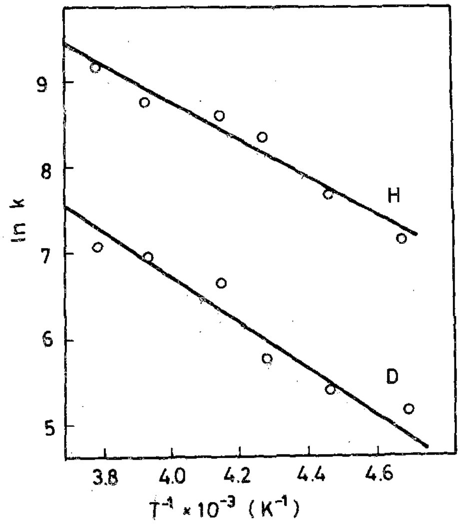

Fig. 2. ln k as a function of T^{-1}

pite the strong dependence of the observed rate on the concentrations, the monomolecular rate constant of proton transfer within the complex is practically unchanged. This indicates that hydrogen bond formation is an intermediate step of the process.

Lifetimes of the states of CD acid complexes were determined from the ^{19}F-NMR spectra. Kinetic parameters of proton and deuteron transfer in the NYFP-TOA complex in comparison with similar values for the DNE-TOA complex are listed in Table 2. Rate constants, extrapolated to the same temperature, in the case of a strong hydrogen bond are considerably higher, whereas the activation energy is significantly lower. Values of the kinetic isotope effect ($k_H/k_D \ngtr 6$) agree with the classical rather than with the tunnel mechanism. This is also supported by the absence of conspicuous deviations of the function ln k vs. T^{-1} from linearity (Fig. 2).

REFERENCES

1. N. D. Sokolov: Dokl. Akad. Nauk SSSR, *60,* 825 (1948).
2. G. S. Denisov, V. M. Schreiber: Spectrosc. Lett., *5,* 377 (1972).
3. P. M. Borodin, N. S. Golubev, G. S. Denisov, N. A. Safarov: Vestn. Leningr. Univ., Fiz. Khim., *4,* 66 (1978).
4. P. M. Borodin, N. S. Golubev, G. S. Denisov, Y. A. Ignatiev: Org. Magn. Reson., *7,* 185 (1975).