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PMR STUDY OF THE LIFETIME OF COMPLEXES WITH A STRONG HYDROGEN BOND AT LOW TEMPERATURES

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The kinetics of formation and cleavage of hydrogen bonds in complexes of carboxylic acids with proton acceptors have been studied by PMR spectroscopy over the range -100 to 150 °C. The activation parameters of the processes have been measured.

По спектрам ЯМР ^{1}H в интервале $-100^\circ \div -155\ ^\circ$C исследована кинетика процессов образования и разрыва водородной связи в комплексах карбоновых кислот с акцепторами протона. Измерены параметры активации этих процессов.

The lifetimes of hydrogen bonds in different complexes in solution have been estimated at room temperature using relaxation techniques /1, 2/ and NMR /3/ methods. These estimates are of the order $10^{-9} - 10^{-10}$ s. The rate of formation and cleavage of these complexes is determined by diffusion, which hinders the measurement of the real activation parameters and the study of the mechanism. The estimates made according to Ref. /4/ indicate that at about -130 °C the lifetimes of stable complexes may reach $10^{-3} - 10^{-2}$ s. A study of the kinetics under these conditions provides significantly more information about the mechanism of formation and cleavage of the hydrogen bond. In the present study an attempt is made to determine the dynamic characteristics of the strong hydrogen bond formed

between carboxylic acids (CF_3COOH, HCOOH) and oxygen-containing acceptors, $(CH_2)_4O$, $(CH_3)_2NCHO$, $(CH_3)_2SO$, $[(CH_3)_2N]_3PO$, at temperatures from -100 to -155°C. The PMR spectra (HR-100 Varian spectrometer and JEOL C-60) of solutions of these substances in CHF_2Cl have been examined. To check the effect of intermolecular proton exchange on the spectrum, we recorded the spectra of strongly dehydrated samples as well as of samples containing some amounts of water. For 0.03-0.2 mol/l HCOOH solutions at -80°C, a separation of the water signal is observed followed by the narrowing of the carboxy proton signal. In the region -120 to -155°C the position of this signal practically does not depend on the temperature and concentration (δ = 13.05$\pm$0.05 ppm). This implies that the molecules are present in the solution almost entirely as cyclic dimers. In the presence of proton acceptors two signals are observed at -150°C: the shift of one of them coincides with that of the dimer signal, the other one is at a lower field and depends on the type of the acceptor (Fig. 1). Thus, under these conditions an equilibrium between $(HCOOH)_2$ dimers and HCOOH... B complexes is observed which may be due to the formation of more complicated complexes. Splitting of the carboxy proton signal into two signals is also observed in the presence of two proton acceptors in the solution. In this case the equilibrium is established between two types of complexes:

$$AH...B' + B'' \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} AH....B'' + B' \qquad (1)$$

For CF_3COOH spectra the addition of an acceptor also leads to signal splitting. However, the lineshape is apparently affected by intermolecular proton exchange (the water signal is separated at -120°C but the effect of exchange with water is not observed below -140°C). The addition of an excess weak acceptor (diethyl ether) strongly inhibits the exchange and thus makes it possible to determine the lifetime of CF_3COOH complexes in equilibrium /1/.

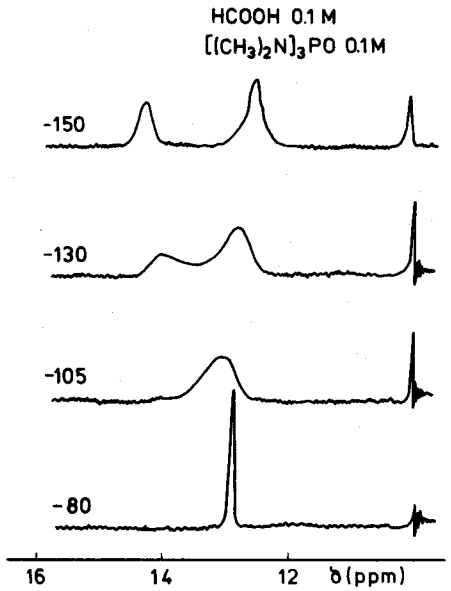

Fig. 1. Spectra of the system containing formic acid and hexamethapol (0.1 mol/1 each) at various temperatures

According to the technique in Ref. /5/, a complete analysis was made of the lineshape of the absorption signal (the relative population of states and the mean lifetime being varied). Chemical shifts of individual forms were found from spectra at the lowest temperature (-155 °C) when the signals were completely separated, time T_2 was determined from the width of the acid signal in the absence of an acceptor. The lifetime thus obtained for the AH...B' complexes, which are in equilibrium with AH...B" complexes is inversely proportional to the concentration of acceptor B". Hence, the rate of exchange of acceptors is first order with respect to both components:

$$V_1 = k_1 [AH...B'] [B''] = [AH...B'] / \tau_{AH...B'}$$

$$V_{-1} = k_{-1} [AH...B''] [B'] = [AH...B''] / \tau_{AH...B''}$$

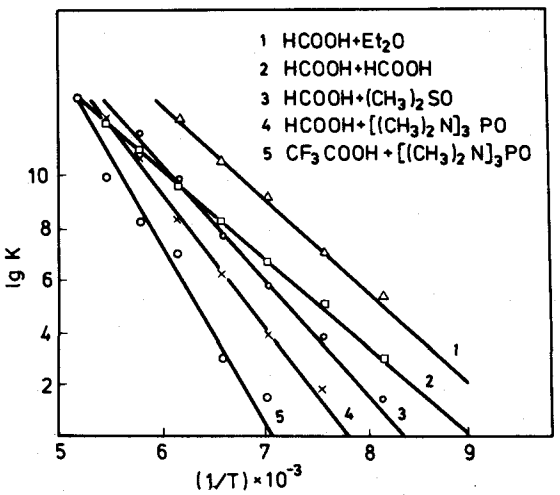

Fig. 2. Logarithm of the rate constant of exchange vs. reciprocal temperature: 1. $HCOOH + (C_2H_5)_2O$; 2. HCOOH + HCOOH; 3. $HCOOH + (CH_3)_2SO$; 4. $HCOOH + [(CH_3)_2N]_3PO$; 5. $CF_3COOH + [(CH_3)_2N]_3PO$

The enthalpy $\Delta H^{\ddagger}$ and entropy $\Delta S^{\ddagger}$ of activation of exchange processes (1) have been determined (Fig. 2) from the temperature dependence of the rate constants, using the method of least squares (diethyl ether was used as acceptor B'). The values obtained are listed in Table 1. The activation energies are rather high and exceed even the values of hydrogen bond energies in such systems /6/. This indicates that the exchange process proceeds via two stages with successive cleavage of one hydrogen bond and formation of another. Since the energy barrier against hydrogen bond formation is apparently close to zero, the level of the transition state differs from the level of free molecules only by the activation energy of diffusion in the liquid. The anomalously high positive activation entropies can be explained by the practical absence of bonding between the molecules in the transition state. The stepwise mechanism of this process is also supported

Table 1

Kinetic characteristics of hydrogen-bonded complexes of formic (HCOOH) and trifluoroacetic (CF_3COOH) acid

Acceptor	HCOOH			CF_3COOH		
	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta H^{\ddagger}$ (kcal/mol)
$(CH_2)_4O$	–	–	–	10.8 ± 0.8	20	10.3
$(CH_3)_2SO$	9.2 ± 0.5	17	7.6	11.3 ± 1.0	24	10.1
$[(CH_3)_2N]_3PO$	10.2 ± 0.8	21	7.3	12.4 ± 1.5	30	10.6
$(CH_3)_2NCHO$	9.8 ± 0.5	20	7.5	12.0 ± 1.5	30	10.6
HCOOH	7.3 ± 0.6	8	–	–	–	–

by the fact that the activation energy of hydrogen bond cleavage in complexes with ether ($\Delta H^{\ddagger}_{eth}$) does not depend on the type of the second acceptor and is probably determined only by the difference between the energy levels of the ether complex and the free molecule.

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