KINETICS OF HYDROGEN BOND FORMATION AND RUPTURE. LIFETIME OF THE $(CF_3)_3COH$ COMPLEX WITH HEXAMETHYLPHOSPHORIC TRIAMIDE IN FREON

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The lifetime of a complex with a hydrogen bond in solution can be determined from the rates of various exchange processes, e.g., exchange with a donor molecule:

$$A'H \ldots B + A''H \rightleftharpoons A''H \ldots B + A'H \tag{1}$$

or a proton acceptor molecule:

$$AH \ldots B' + B'' \rightleftharpoons AH \ldots B'' + B'. \tag{2}$$

A proton donor can participate in exchange with self-associates:

$$(AH)_2 + 2B \rightleftharpoons 2AH \ldots B. \tag{3}$$

The lifetime of a complex determined from such equilibria generally depends in a complicated way on the concentration of components. From the viewpoint of hydrogen bond theory there is a great deal of interest in a lifetime determined by the monomolecular dissociation of a complex:

$$AH \ldots B \underset{k}{\overset{k_D}{\rightleftharpoons}} AH + B, \tag{4}$$

which is the fundamental characteristic of kinetic bond strength. One of the central questions is whether type (1), (2), (3) exchange reactions proceed by way of successive rupture of one hydrogen bond and formation of another, or cooperatively through a transition state with several bonds. The kinetics of molecular exchange (2) was studied in [1] for a number of systems, and on the basis of an analysis of kinetic parameters a stepwise process was proposed. In the present work the kinetics of reactions (4) and (2) are directly compared by means of low-temperature dynamic NMR [2] for the same complex with a hydrogen bond. Measurement of the dissociation rate of complexes is limited by the tendency of most strong proton donors to undergo self-association. At low temperatures and not too low concentrations this complicates the equilibria in the system. In this work we chose as proton donor tertiary-nonafluorobutanol, $(CF_3)_3COH$ (NFB), the proton-accepting tendency of which is extremely small. Consequently, despite a very high proton-donating tendency [3], at concentrations below 10^{-2} M this alcohol is practically unassociated. As proton acceptor we used hexamethylphosphorictriamide (HMPT).

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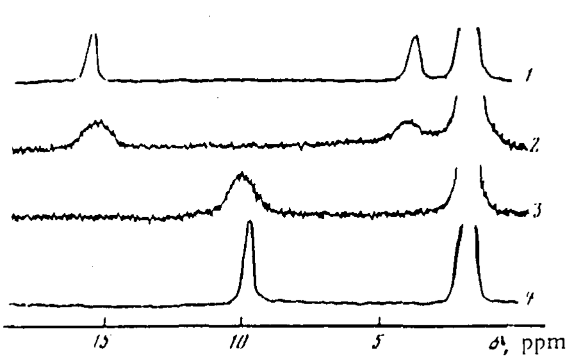

Fig. 1. NMR spectra of solution of 0.01 M NFB and 0.005 M HMPT in CDF_2Cl_2–$CDFCl_2$ mixture at 1) −153, 2) −133, 3) −113, and 4) −73°C.

The NFB sample was purified by vacuum distillation at −30°C over 4A zeolite. Analytically pure grade HMPT was held over 13X zeolite for several days, then distilled at 20 Pa pressure in a current of dry argon. It was then molecularly distilled at room temperature and condensed on a liquid-nitrogen-cooled surface. As solvent suitable for obtaining NMR spectra down to temperatures of the order of 100°K, we used a mixture of Freons CDF_2Cl and $CDFCl_2$, obtained by fluorination of $CDCl_3$ (99.6% isotopic purity) by the method of [4] and dried by repeated vacuum distillation at −60°C. Glass ampuls precalcined in vacuum were filled in a box in a dry argon atmosphere, attached to a vacuum apparatus, cooled with liquid nitrogen, and evacuated to 10^{-2} Pa; then the solvent was distilled into them. The ampuls were sealed off from the vacuum apparatus and placed in a spectrometer detector (JEOL C 60 HL or Bruker HX90). This procedure assured a reproducibility of the chemical shift signal of the OH proton within 0.03 ppm.

Figure 1 shows the spectra of a solution containing HMPT and excess NFB at various temperatures. At 110°K there are two narrow signals; the low-field signal coincides with the signal of the OH proton in the solution containing a large excess of HMPT, and consequently belongs to the AH...B complex. The high-field signal belongs to free NFB molecules; its chemical shift coincides with that of a solution containing only NFB at less than 10^{-2} M (it is practically independent of temperature, which indicates the absence of self-association). When the relative concentrations of components are changed, the intensity of the signals changes, but not their position. When the temperature is raised the signals broaden and collapse. The averaging of the signals may be due to process (4), formation and dissociation of complexes; or degenerate exchange (1), where A'H and A"H are identical molecules; or finally to proton exchange between AH...B. But the shape of the lines does not change when the solution is diluted 20-fold at a given starting rotation of $[\Delta H]_0$ and $[B]_0$. This is a strong argument in favor of reaction (4); any process that required collision of a complex with AH, B, or AH...B would show a dependence of lifetime on absolute concentration. Since equilibrium (4) is strongly displaced to the left at low temperatures, in the presence of excess AH the concentration of free B is negligibly small in comparison with [AH] and [AH...B], and for process (4) we have

$$t_{\mathrm{AH}\ldots\mathrm{B}} = k_{\mathrm{D}}^{-1},$$
$$t_{\mathrm{AH}} = k_a^{-1}[\mathrm{B}]^{-1} = Kk_a^{-1}[\mathrm{AH}][\mathrm{AH}\ldots\mathrm{B}]^{-1} \approx Kk_a^{-1}([\mathrm{AH}]_0/[\mathrm{B}]_0 - 1), \quad (5)$$

where K is the equilibrium constant of (4). The lifetimes t_{AH} and $t_{AH\ldots B}$ are independent of the absolute concentrations. By line-contour analysis one may easily obtain information on the rates of hydrogen bond rupture. Finding k_a, however, requires knowledge of the equilibrium constant K that has a very large value. It can be measured at very high temperatures, where equilibrium (4) is not displaced so strongly to the left, and then extrapolated (in a plot of ln K vs. T^{-1}) to the 110-170°K region. At 170-210°K, K has been determined from the concentration dependence of the chemical shift of the averaged signal of the OH proton (in excess HMPT) by the procedure described in [5]. In this case δ_K, the chemical shift of the complex, and K were varied, and δ_M, the chemical shift of the monomer, was measured directly. The calculated δ_K for the 170-210°K range is 15.1 ± 0.3 ppm, while the

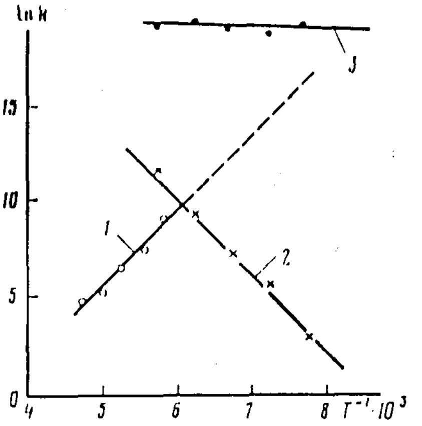

Fig. 2

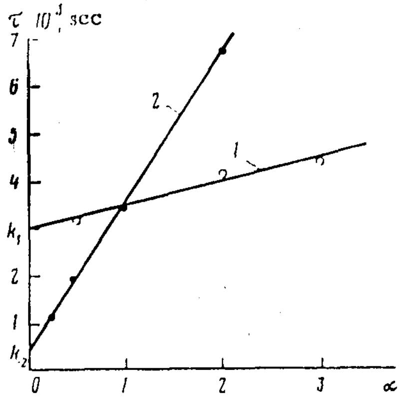

Fig. 3

Fig. 2. Temperature dependence of logarithm of 1) equilibrium constant K, 2) dissociation rate constant k_D, and 3) formation constant of HFB—HMPT complex k_a.

Fig. 3. Dependence of measured lifetimes of the HFB—HMPT complex 1) and HFB with $(CH_3)_2O$, 2) complexes on the ratio of concentrations of α complexes.

measured value at 110°K is 15.4 ± 0.04 ppm (Fig. 1). The dependences of the constants K, k_D, and k_a are presented in Fig. 2. The enthalpy of complex formation is 32 ± 2 kJ/mole; the activation energy of hydrogen bond rupture E_D^* = 36 ± 3 kJ/mole. The anomalously high preexponential factor in the Arrhenius equation (log A = 16 ± 0.1) is noticeable. Such an effect has been observed previously for some monomolecular ruptures; it is explainable by the fact that when the bond is substantially weakened in the transition state, the frequencies of the intermolecular oscillations are sharply reduced and the oscillational statistical sums are increased. The activation energy of complex formation is close to zero ($E_a^{\ddagger}$ = 3 ± 2 kJ/mole). We note that despite hydrogen bond formation the surmounting of any noticeable energy barrier is not involved, and the rate constant ($k_a \approx 3 \cdot 10^8$ liter/mole·sec) is substantially less than the value determined from the diffusion limit ($\sim 10^{10}$ liter/mole·sec). This is probably to be attributed to a steric factor, since complex formation requires the collision of two polyatomic molecules oriented in a particular way.

The kinetics of exchange (2) by NFB molecules between complexes with HMPT and with dimethyl ether was studied further: B″ = $(CH_3)_2O$, and B′ = $[(CH_3)_2N]_3PO$. The spectra of solutions of NFB, HMPT, and excess ether are completely analogous to those shown in Fig. 1, but instead of the signal of the free alcohol molecules (δ = 4.4 ppm), there appears the signal δ = 10.6 of the $(CF_3)_3COH\ldots O(CH_3)_2$ complex. In this case the line shape is strongly dependent on component concentration.

If exchange (2) proceeds with simultaneous rupture of one hydrogen bond and the formation of another:

$$AH\ldots B' + B'' \overset{k}{\rightleftharpoons} \left[AH \begin{matrix} \cdot\cdot\, B' \\ \cdot\cdot\, B'' \end{matrix} \right] \underset{k_{-1}}{\rightleftharpoons} AH\ldots B'' + B', \tag{6}$$

then the measured lifetime of the complex, $\tau_{AH\ldots B'}$, must be inversely proportional to the concentration of free B″:

$$\tau_{AH\ldots B'} = k_1^{-1}[B'']^{-1} = k_1^{-1}K[B']^{-1}[AH\ldots B'][AH\ldots B'']^{-1}. \tag{7}$$

With increasing excess of B″, equilibrium (6) shifts to the right, the ratio [AH...B′]/[AH...B″] approaches zero, and B″ approaches the initial concentration B_0, so that the lifetime $\tau_{AH\ldots B}$ also approaches zero.

In this case, if the molecular exchange includes successive steps of rupture of one bond and formation of another:

$$AH\ldots B' + B'' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AH + B' + B'' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AH\ldots B'' + B' \tag{8}$$

and if the rupture is the limiting step, then the forward reaction rate will be

$$v = k_1[\mathrm{AH}\ldots\mathrm{B}']\frac{k_2[\mathrm{B}'']}{k_2[\mathrm{B}'']+k_{-1}[\mathrm{B}']} = k_1[\mathrm{AH}\ldots\mathrm{B}']\left(1+k_1k_{-2}^{-1}\frac{[\mathrm{AH}\ldots\mathrm{B}']}{[\mathrm{AH}\ldots\mathrm{B}'']}\right)^{-1}.$$

An analogous reaction can be written for the reverse reaction. Since the average lifetime of state X at equilibrium is $[X]v^{-1}$, the observed lifetimes of the complexes will be

$$\tau_{\mathrm{AH}\ldots\mathrm{B}'} = k_1^{-1}\left(1+\frac{k_1}{k_{-2}}\,\frac{[\mathrm{AH}\ldots\mathrm{B}']}{[\mathrm{AH}\ldots\mathrm{B}'']}\right),$$

$$\tau_{\mathrm{AH}\ldots\mathrm{B}''} = k_{-2}^{-1}\left(1+\frac{k_{-2}}{k_1}\,\frac{[\mathrm{AH}\ldots\mathrm{B}'']}{[\mathrm{AH}\ldots\mathrm{B}']}\right). \qquad (9)$$

The ratio of complex concentrations can be obtained simultaneously with the average lifetime in the analysis of signal shapes. If the reaction goes according to mechanism (8), then the relationships of $\tau_{\mathrm{AH}\ldots\mathrm{B}'}$ and $\tau_{\mathrm{AH}\ldots\mathrm{B}''}$ to the ratio of complex concentrations [AH...B']/[AH...B"] and [AH...B']/[AH...B'], respectively, must be linear. In contrast to mechanism (6), when equilibrium (2) shifts to the right the lifetime $\tau_{\mathrm{AH}\ldots\mathrm{B}'}$ does not approach zero, but rather $k_1^{-1} = k_D^{-1}$.

Figure 3 presents these relationships at 140°K; the intercept of the straight line $\tau_{\mathrm{AH}\ldots\mathrm{B}'} = f([\mathrm{AH}\ldots\mathrm{B}']/[\mathrm{AH}\ldots\mathrm{B}''])$ is close to the value of k_D^{-1} measured for reaction (4).

The experimental (k_D) and the calculated (k_1) rate constants for the dissociation of the NFB—HMPT complex, and also the calculated constants (k_{-2}) for the dissociation of the NFB—dimethyl ether complex, are as follows:

T, K	120	130	140	150	160	170
k_D, sec^{-1}	–	29	$3.0\cdot10^2$	$2.5\cdot10^3$	$1.6\cdot10^4$	$7.0\cdot10^4$
k_1, sec^{-1}	–	32	$3.2\cdot10^2$	$3.1\cdot10^3$	$1.3\cdot10^4$	$8.6\cdot10^4$
k_{-2}, sec^{-1}	28	$3.4\cdot10^2$	$2.0\cdot10^3$	$1.1\cdot10^4$	$4.5\cdot10^4$	$2.1\cdot10^5$

The practically complete coincidence of k_1 and k_D substantiates the stepwise mechanism of molecular exchange (2). Consequently, to determine the kinetic characteristics of complex dissociation we may use the lifetimes measured in the presence of an excess of a proton acceptor. Since under such conditions as a rule only one equilibrium (2) is established, such a determination is also feasible for proton donors that tend to self-associate, such as carboxylic acids and phenols.

In conclusion, it is interesting to compare the lifetimes of intermolecular hydrogen bonds with the analogous values for intramolecular bonds obtained in [7]. Kinetically the intramolecular bonds are significantly more stable than the intermolecular; thus the intramolecular bond lifetime in salicylaldehyde with 30 kJ/mole energy [8] at 170°K is $2\cdot10^{-2}$ sec, which is three orders of magnitude larger than that of the complex studied in the present work (32 kJ/mole). This is probably related to the fact that during rupture of the intramolecular bond, a rigid molecular configuration is retained, and the vibrational statistical sums do not increase significantly in the transition state.

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