SPECTROSCOPIC STUDY OF THE RATE OF ISOTOPIC EXCHANGE OF THE HYDROGEN IN ALCOHOLS AND AMINES WITH MERCAPTANS IN SOLUTION

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Infrared spectroscopy was used to measure the rate of isotopic exchange of the hydrogen in the OH group of alcohols and the NH group of amines with the SH group of mercaptans in CCl_4 solution. The kinetics of the process conforms to a bimolecular law. The rate constants for the exchange are compared with the ability of alcohols and amines, as proton donors and acceptors, to form hydrogen bonds. The activation energies for exchange were found. The results are discussed in the framework of the concept of a cooperative transfer of protons in a cyclic complex involving hydrogen bonds.

Studies have been carried out [1-3] of the kinetics of proton exchange in groups having the ability to form a hydrogen bond either by acting as a donor or acceptor of a proton. It has been found that hydrogen in the SH group is exchanged much more slowly than in the OH group. These results are in accord with the hypothesis that the rate constant for isotopic exchange of hydrogen in such systems is determined by the same features in the electronic structure of XH groups which enable them to form hydrogen bonds, and support the hypothesis that the exchange mechanism involves the transfer of protons in a cyclic complex containing hydrogen bonds. In order to investigate further the effects of the electronic structure of molecules on the characteristics of cooperative proton transfer, the present work was devoted to a study of the kinetics of isotopic hydrogen exchange in a series of compounds with systematically changing donor and acceptor properties. As the analysis of the experimental results shows, the proton donor ability of an XH group forming an XH ... Y bond is determined by the electronically unscreened nature of the proton, while the proton acceptor (electron donor) ability of Y depends on the density of the electron cloud of the free pair.

TABLE 1. Kinetic Characteristics of Hydrogen Exchange in Alcohol – Mercaptan Systems

System	Reaction order		$k^*_{exp} \cdot 10^2$	$k^*_{bi} \cdot 10^2$, liter /mole·sec	ΔE, kcal/mole
	in alcohol, α	in mercaptan, β			
$CH_3OH + $ tert-C_4H_9SD	$1,4\pm0,1$	$0,9\pm0,2$	$8,9\pm0,2$	$7,0\pm2,0$	$3,0\pm0,3$
$C_2H_5OH + $ tert-C_4H_9SD	$1,4\pm0,2$	$1,0\pm0,2$	$2,4\pm0,2$	$2,2\pm0,4$	$5,0\pm1,0$
iso $C_3H_7OH + $ tert-C_4H_9SD	$1,7\pm0,4$	$1,0\pm0,2$	$1,2\pm0,2$	$0,9\pm0,4$	$5,5\pm0,8$
tert-$C_4H_9OH + $ iso-C_4H_9SD	$1,2\pm0,2$	$1,1\pm0,2$	$0,65\pm0,04$	$0,4\pm0,2$	$5,0\pm1,0$
$CF_3CH_2OH + $ iso C_4H_9SD	$1,4\pm0,1$	$0,8\pm0,2$	10 ± 1	3 ± 1	—
$CH_3OH + $ iso-C_4H_9SD	$1,3\pm0,2$	$1,4\pm0,5$	23 ± 6	3 ± 2	—
iso $C_3H_7OH + $ iso-C_4H_9SD	$1,29\pm0,01$	$1,4\pm0,3$	$2,2\pm0,4$	$0,4\pm0,2$	—
tert-$C_4H_9OH + $ iso-C_4H_9SD	$0,8\pm0,1$	$1,6\pm0,2$	$0,67\pm0,08$	$0,4\pm0,2$	—

*k_{exp} is the rate constant calculated from experimental values of the reaction order; k_{bi} is the rate constant calculated assuming $\alpha = \beta = 1$.

TABLE 2. Kinetic Characteristics of Hydrogen Exchange in Amine—Mercaptan Systems

System	Reaction order		$k^{*}_{exp} \cdot 10^2$	$k^{*}_{bi} \cdot 10^2$, liter/mole ·sec	ΔE, kcal/mole
	in amine, α	in mercaptan, β			
(C$_2$H$_5$)$_2$NH+ tert-C$_4$H$_9$SD	1,2+0,4	1,08+0,09	2,0+0,4	1,1+0,4	6,0+1,0
(n-C$_3$H$_7$)$_2$NH+ tert-C$_4$H$_9$SD	1,2±0,3	1,3±0,2	3,2±0,3	0,84±0,06	8,0±2,0
(iso-C$_4$H$_9$)$_2$NH+ tert-C$_4$H$_9$SD	0,9±0,2	0,95±0,09	0,27±0,05	0,37±0,09	8,0±2,0
(C$_2$H$_5$)$_2$NH+iso-C$_4$H$_9$SD	1,41±0,06	1,2±0,1	5,2±0,4	0,8±0,2	—
(n-C$_3$H$_7$)$_2$NH+iso-C$_4$H$_9$SD	0,9±0,2	1,4±0,3	0,42±0,07	0,23±0,09	—
(iso-C$_4$H$_9$)$_2$NH+ iso-C$_4$H$_9$SD	1,0±0,2	1,1±0,1	0,16±0,03	0,16±0,03	—
(C$_6$H$_5$)$_2$NH+iso-C$_4$H$_9$SD	0,6±0,3	1,0±0,4	0,9±0,2	0,6±0,2	—
(C$_6$H$_5$)$_2$NH + tert-C$_4$H$_9$SD	1,2±0,3	1,1±0,2	0,18±0,03	0,10±0,03	6,0±2,0

* See footnote to Table 1.

Infrared absorption spectra were used to study the rate of proton exchange between the SH group of butyl mercaptans and the OH and NH groups of alcohols and secondary amines in CCl$_4$ solutions at different concentrations and temperatures. The alcohols considered were CH$_3$OH, C$_2$H$_5$OH, iso-C$_3$H$_7$OH, and tert-C$_4$H$_9$OH, in which, with an increase in the number of methyl groups replacing the hydrogen atoms in the methanol molecule, there is an increase in the electron density in the region of the free electron pairs on the oxygen atom and a decrease in the excess positive charge on the hydroxyl hydrogen atom. In the series of amines studied, (C$_2$H$_2$)$_2$NH, (n-C$_3$H$_7$)$_2$NH, and (iso-C$_4$H$_9$)$_2$NH, there was also an increase in the proton acceptor, and decrease in the proton donor, properties of the NH group, owing to the positive inductive effect of the aliphatic radicals. The ionization potential, defined as the energy necessary to remove a free pair electron, is a good quantitative indicator of the proton acceptor ability within a given class of compounds. In the series of alcohols investigated, the ionization energies are 10.85, 10.50, 10.15, and 9.70 eV, respectively [4]. This indicates a systematic increase in the proton acceptor ability. Any decrease in the proton donor ability of the alcohols in this series can be judged from studies [5,6] in which measurements were made of the hydrogen bond energy in complexes of alcohols with the same proton acceptors, together with determinations of the band shift ν(OH). Values of the energy of the hydrogen bond formed by secondary amines acting either as proton donors or acceptors [7] also indicate a change in the electron and proton donor ability of the NH group according to the inductive effect of the substituent.

The work was carried out on IKS-11 and IKS-12 spectrometers with OAP-1 detectors, and a PbSe photoconductive cell cooled with liquid oxygen. The time constant of the detector —recorder system was in all cases at least an order of magnitude smaller than the reaction time of the fastest reactions. The reagents were mixed by injecting one of the solutions directly into an optical cuvette containing the second solution. Oscillographic measurements showed that the mixing time was less than 1 sec. The thickness of the absorbing layer was varied from 3-50 mm. The spectral slit width was 5-8 cm^{-1}. During an experiment the changes with time of the absorption band intensities for the valence vibrations of the OH, OD, NH, and SH groups were recorded. Using the familiar relationships [8]

$$1 - F = \frac{D_\infty - D_t}{D_\infty - D_0} = e^{-rt}, \qquad R = \frac{r}{[A] + [B]}[A][B],$$

where [A] and [B] are component concentrations, F is the fraction exchanged, D_0, D_t, and D_∞ are the optical densities of the absorption bands at t = 0, t, and ∞, calculations were made of the exchange rate R, which is independent of time. The rate R is related to the true rate of the hydrogen exchange reaction Q by the equation

$$R = Q/g,$$

where g is a parameter allowing for the isotope effect associated with the nonideality of the label.

Tables 1 and 2 give the results of measurements of the rates of hydrogen exchange for the alcohols CH$_3$OH, C$_2$H$_5$OH, iso-C$_3$H$_7$OH, tert-C$_4$H$_9$OH, and CF$_3$CH$_2$OH at concentrations C = 0.001-2 moles/liter, and the amines (C$_2$H$_5$)$_2$NH, (n-C$_3$H$_7$)$_2$NH, (iso-C$_4$H$_9$)$_2$NH, and (C$_6$H$_5$)$_2$NH at C = 0.01-0.5 moles/liter with the mercaptans tert-C$_4$H$_9$SD and iso-C$_4$H$_9$SD at C = 0.01-4 moles/liter. The mercaptans contained ~80% deuterium in the sulfhydryl group. Values of the rate constant k_{exp} at 24°C and the reaction orders in alcohol (amine), α, and mercaptan, β, were obtained using the least squares method to solve the system of equations

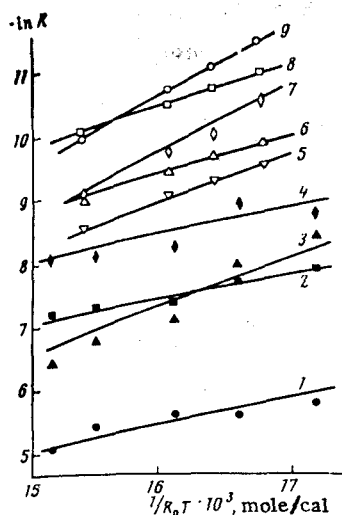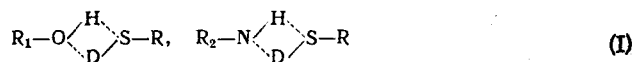$$\ln R_i = \ln k_{exp} + \alpha \ln A_i + \beta \ln B_i,$$

Fig. 1. Determination of activation energies for hydrogen exchange at various component concentrations: 1-4) tert-C_4H_9SD + tert-C_4H_9OH; 5-9) tert-C_4H_9SD + $(n-C_3H_7)_2NH$.

where R_i is the experimentally measured value of the rate at component concentrations A_i and B_i. The number of equations in each system was not less than 10. The values of α and β were usually close to unity. This makes it possible to consider the process as bimolecular and the exchange a synchronous transfer of protons in cyclic complexes containing hydrogen bonds:

$$R_1-O\diagdown^{H}_{\diagdown D}\diagup S-R, \quad R_2-N\diagdown^{H}_{\diagdown D}\diagup S-R \qquad (I)$$

Average values of the rate constant k_{bi}, calculated on the basis of $\alpha = \beta = 1$, are given in the tables.

In analyzing the change in the exchange rate in a series of compounds, it is necessary to take into account the fact that the stability of cyclic complex I is determined by the total energy of the two hydrogen bonds. The energies of these bonds in a series of amines or alcohols change in opposite directions, such that the stability of the complex changes in these series less than does the stability of each bond. Unfortunately it is not possible to make direct spectroscopic measurements of the energies of type I complexes, since it is impossible to identify the spectral bands belonging to the cyclic associates. It is therefore necessary to assess the role of the proton donor and acceptor capabilities of XH groups in the exchange kinetics only from experimental values of the reaction rates. From the tables it is seen that increasing the proton donor capability of the XH group in a series of alcohols and amines leads to increases in k_{exp} and k_{bi}. The sole exception, k_{exp} for the system $(n-C_3H_7)_2NH$ + tert-C_4H_9SD, is caused by a marked departure of the reaction orders from unity.

In addition to the aliphatic alcohols, trifluoroethanol was studied. Its proton donor ability is appreciably greater than that of unlabeled alcohols, but the measured rate is no greater than that of methanol. It is difficult to say definitely whether this is associated with an intrinsic decrease in the proton acceptor ability of the hydroxyl group, or an effect arising from the large difference in the experimental values of α and β for these two alcohols. The aromatic amine $(C_2H_5)_2NH$ behaves in an analogous way. The hydrogen exchange rate of diphenyl amine with mercaptans was of the same order of magnitude as in systems with aliphatic amines, although the proton donor abilities of the latter are substantially lower [7]. In the case under consideration the effect is undoubtedly caused by a reduction in the electron donor ability of the free electron pair on the nitrogen atom, arising from its coupling with the π-electrons. Therefore the exchange occurs in a cyclic complex having two hydrogen bonds differing greatly in stability and giving rise to a rate for the process which is sufficiently low. The values of the parameters for the exchange reactions in which tert-butyl and iso-butyl mercaptans participate are similar. This result is reasonable, since the proton donor and acceptor capabilities of the SH groups in these compounds differ only slightly.

Summing up, all the substances studied can be placed in a series according to their decreasing rates of hydrogen exchange with mercaptans: $CH_3OH > C_2H_5OH > (C_2H_5)_2NH > iso-C_3H_7OH \gtrsim (n-C_3H_7)_2NH \approx tert-C_4H_9OH > (iso-C_4H_9)_2NH$.

The activation energies, ΔE, were determined from plots of ln R versus $1/R_0T$. In each system exchange rates were measured for five different concentrations of components at four or five temperatures in the 6-60°C range. Under these conditions no systematic deviations from the Arrhenius equation were observed, and the plots of ln R versus $1/R_0T$ were approximately linear. Typical results obtained for several of the systems are shown in Fig. 1. From the tables it follows that in the series of amines and alcohols ΔE is close to one. Comparing these values with other work [2] it can be seen that the activation energy for exchange of alcohols and amines with mercaptans is appreciably lower than the value of ΔE (13 kcal/mole) for the isobutyric acid — isobutyl mercaptan system. This can be explained on the basis of a cooperative transfer of protons in a four-center cyclic complex. Such a process is not associated with a substantial reorganization of the electron cloud of the partners, as in a carboxylic acid, and requires a lower activation energy.

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