USE OF INFRARED SPECTROSCOPY TO MEASURE THE RATE OF THE ISOTOPIC EXCHANGE OF HYDROGEN BETWEEN MOLECULES OF ALCOHOL AND THIOL

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In the isotopic exchange of hydrogen in XH bonds (X represents an atom with unshared electron pairs), an important role is played by the transfer of protons in a cyclic complex with hydrogen bonds [1]. Data obtained by the EPR method show that the process is catalyzed by acids and bases, and the value of the rate constants for reactions involving ions are higher by several orders of magnitude than those for reactions involving neutral molecules [2, 3]. This last type of reaction is most conveniently studied in the gaseous phase or in solution in an inert solvent. The use of NMR under these conditions is associated with considerable technical difficulties, and infrared spectroscopy might be of considerable use in this connection. An attempt to use infrared spectroscopy to study the kinetics of the isotopic exchange of hydrogen in the hydroxyl group of alcohols and water in the gaseous phase [4] was unsuccessful, however. The authors [4] could only state that the equilibrium distribution of the isotopes is complete in less than 20 sec.

In the present work, we chose as one of the reaction partners a thiol, RSH. We studied the exchange reactions of methanethiol and 2-methylpropanethiol with d-methanol in the gaseous phase and of d-2-methylpropanethiol with methanol and acetic acid in solution in CCl_4. The reactions were carried out in glass absorption cells with LiF and CaF_2 windows at room temperature, 26 ± 2° C. In the gaseous phase, the experiments were carried out at a pressure of the components equal to 20–80 mm Hg in a cell with a length of 19 cm; in the experiments with the solutions, the concentrations were varied in the ranges 0.003–0.08 M for the alcohol, 0.002–0.004 M for the acid, and 0.003–0.1 M for the thiol, with cell thicknesses in the range 1–5 cm. The kinetics of the reaction were measured from the change in the intensity of the ν(OH) and ν(OD) absorption bands with time (see the figure). The experiments were carried out with IKS-12 instruments with an LiF prism and an OAP-1 receiver, and with a modified IKS-6 instrument [5].

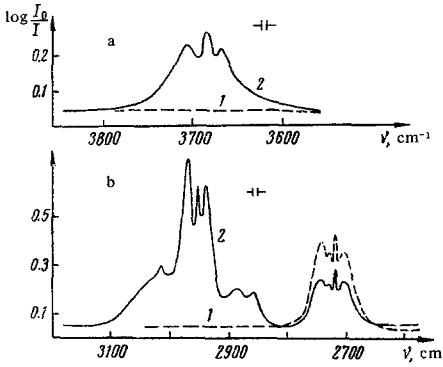
The first experiments showed that the equilibrium distribution of the isotopes in the system is established in 1–30 min, so that the kinetics of the process can be followed fairly accurately. The process obeys the exponential law

$$[\mathrm{OH}]_t = [\mathrm{OH}]_\infty + ([\mathrm{OH}]_0 - [\mathrm{OH}]_\infty)\, e^{-rt},$$

where the experimentally measured value of r is related to the rate of isotopic exchange R by the expression [6]

$$R = r\left(\frac{1}{[\mathrm{OH}]+[\mathrm{OD}]} + \frac{1}{[\mathrm{SH}]+[\mathrm{SD}]}\right)^{-1}.$$

This relationship is correct when the isotope effect is neglected. The values of r measured from the ν(OH) and ν(OD) bands differ by 15–20%.



Absorption spectra of a mixture of CH_3SH and CD_3OD vapor in the region of: ν(OH) ~ ~ 3680 cm^{-1} (a); ν(CH) ~ 2950 cm^{-1}; and ν(OD) ~ 2720 cm^{-1} (b): 1) spectrum of CD_3OD vapor; 2) spectrum of a mixture of CD_3OD + CH_3SH vapor in a state of isotopic equilibrium. Partial pressure of the components 40 mm Hg.

Comparison of the results obtained with published data [4] shows that in the gaseous phase an exchange reaction of the type

$$R\,\mathrm{OH} + R\,\mathrm{SH}^* \rightarrow R\,\mathrm{OH}^* + R\,\mathrm{SH}$$

takes place more slowly than the exchange of hydrogen between hydroxyl groups. Thus, at a methanol pressure of 80 mm Hg and a methanethiol pressure of 40 mm Hg, the rate of isotopic exchange, measured from the ν(OH) and ν(OD) bands, has the values 10.5 and $9.5 \cdot 10^{-6}$ mole/l·sec respectively (half-exchange time 150 sec).

According to spectroscopic data [7, 8], thiols form weaker hydrogen bonds with either the hydrogen atom or the sulfur atom, when compared with hydroxyl compounds of analogous structure, even though the thiols are stronger acids. From this it follows that the rate of isotopic exchange depends primarily on those features of the structure of the electron clouds of the molecule partners which determine the proton-donating and proton-accepting power of the exchanging groups in hydrogen bond formation.

Measurement of the rate of exchange of methanol and acetic acid with d-2-methylpropanethiol in CCl_4 solution shows that the exchange with the acid is faster by almost two orders of magnitude than that for the alcohol. The average values of the rate constants, calculated on the assumption that the process is bimolecular, are $3.5 \cdot 10^{-2}$ and 2.5 l/mole • sec for the methanol–2-methylpropanethiol and acetic acid–2-methylpropanethiol systems, respectively. The marked increase in the rate of isotopic exchange on going from methanol to acetic acid agrees with the increase in the proton-donating power of the OH group, and provides further evidence in support of the suggestion that the elementary act of isotopic exchange is the simultaneous transfer of protons in a cyclic complex with hydrogen bonds.

The kinetics of isotopic exchange between methanol and 2-methylpropanethiol were also measured in the gaseous phase. It was found that approximately equal rates of exchange are observed at concentrations of the components in the gaseous phase which are smaller by factors of 5–10 than those in solution, i. e., exchange takes place more slowly in solution than in the gaseous phase. This result can be understood on the basis of published data [9], according to which, increase in the energy of the reaction of hydroxyl-containing molecules with a solvent leads to an increase in the lifetime of the proton between the two acts of exchange. On going from the gaseous phase to the solution in CCl_4, the energy of the proton-donating molecules is lowered by a considerable amount [10], and this apparently explains the decrease in the rate of isotopic exchange of hydrogen.

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