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EFFECT OF INTRAMOLECULAR HYDROGEN BONDING ON THE KINETICS OF FAST HYDROGEN EXCHANGE

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The kinetics of hydrogen exchange between phenol derivates and methanol have been followed in CCl_4 solution by IR spectroscopy, using a multicapillary mixer with a time resolution of 3 msec. The influence on the rate of the electronic structure and the ability to form intra- and intermolecular hydrogen bonds is discussed.

Методом кинетической ИК-спектроскопии с использованием струевого жидкостного смесителя с временным разрешением 3 мсек изучена кинетика процессов водородного обмена замещенных фенолов со спиртом в CCl_4. Обсуждено влияние электронного строения молекул и их способности к образованию внутрии межмолекулярных водородных связей на скорость реакции.

The kinetics of proton exchange processes involving the hydroxyl groups of phenol or substituted phenols have been studied by NMR. Hydrogen exchange between phenolic and alcoholic hydroxyl groups in binary systems /1, 2/ has been shown to be very fast. This fact impedes the study of hydrogen exchange kinetics by optical spectroscopy because of the relatively large recording time which determines the time resolution of standard spectral instruments. The main advantage of spectroscopic methods is the possibility to study the reaction under conditions minimizing interactions with the medium (dilute solutions in inert solvents or in the gas phase), which is important in elucidating the process and its elementary

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steps. The IR apparatus /3/ devised for the measurement of fast processes in liquids by the stopped-flow technique permits to study the kinetics of H-exchange between alcohols and secondary amines in solution in the time range of 0.03 – 1 sec /4/.

In the present paper we report on the study of the H-exchange process $ROH + CH_3OD \rightleftharpoons ROD + CH_3OH$ in CCl_4 (where ROH-phenol, p-chlorophenol, o-chlorophenol and 2,4,6-trichlorophenol) by kinetic IR-spectroscopy. These models permit to examine the effect of the electronic structure of the molecules and their ability to form intra- and intermolecular hydrogen bonds on the kinetics of the reaction. The processes were followed by measuring the dependence of the intensity on time at the absorption maxima of phenolic OH and OD stretching vibrations. These changes correspond to the redistribution of deuterium between the hydroxyl groups of the molecules. The spectral changes during the exchange of deuteromethanol (deuterium content of the hydroxyl group not lower than 90%) with phenol and o-chlorophenol are shown in Figs. 1 and 2, respectively; for p-chlorophenol and $2,4,6\text{-}Cl_3C_6H_2OH$ the spectra were similar to those shown in Figs. 1 and 2, respectively. The strong decrease in the frequency of the ν_{OH} and ν_{OD} bands in Fig. 2 can be explained by intramolecular H-bonding between the hydroxyl group and the Cl atom in ortho-position.

The reagents were mixed in a multicapillary flow mixer with a time resolution of 3 msec; the kinetic curves were photographed from the oscillograph screen at a time base of 0.1–1 sec. The optical path was 2 mm; the phenol and methanol concentrations were varied in the interval of 0.1–0.01 mol/l. Usually 15–23 experiments were performed at different concentrations at 20 and 50 °C. Known formulas /5/ were used to calculate the rates (r) at which the system approaches the equilibrium isotope distribution. From these values the specific rates (R) and

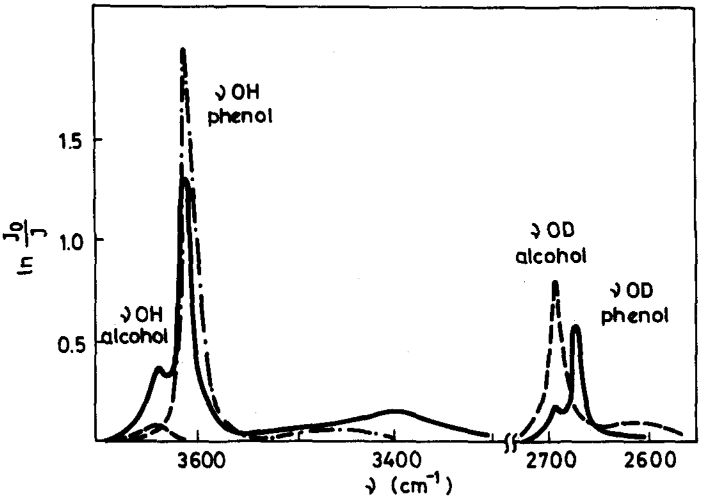


Fig. 1. Spectra of systems 0.05 mol/l CH_3OD + 0.02 mol/l C_6H_5OH in CCl_4 before (dotted line) and after (solid line) H-exchange

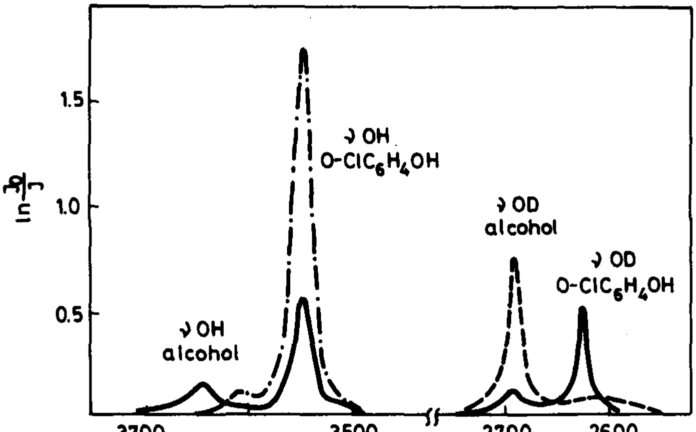


Fig. 2. Spectra of systems 0.05 mol/l CH_3OD + 0.02 mol/l $o\text{-}ClC_6H_4OH$ in CCl_4 before (dotted line) and after (solid line) H-exchange

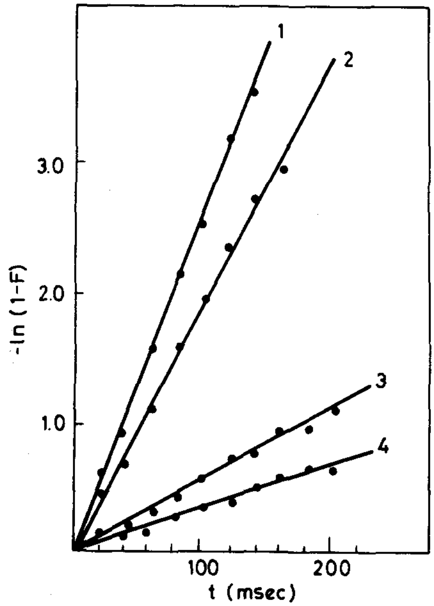
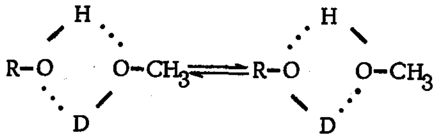


Fig. 3. Kinetics of H-exchange in 0.02 mol/l CH_3OD + 0.06 mol/l ROH systems in CCl_4 at 20 °C; 1 - p-ClC_6H_4OH; 2 - C_6H_5OH; 3 - o-ClC_6H_4OH; 4 - 2,4,6-$Cl_3C_6H_2OH$

the orders with respect to phenol (α) and alcohol (β) have been calculated to obtain the number of molecules involved in the rate-determining step. The Arrhenius activation energies E_a were determined from the ln k vs. $1/R_0T$ plots (where k is the rate constant of H-exchange). The data were evaluated by the least squares method.

The results show that the kinetics of the reactions studied obey the exponential law 1−F = exp(−rt), where 1−F is the fraction exchanged (Fig. 3). The R values are proportional to the concentration of both reactants at all concentrations and temperatures used. The α and β values are close to unity (rms deviation ±0.2). Thus, one can draw the conclusion that the processes studied are bimolecular, which is typical for most H-exchange reactions in solution. The data obtained are listed in Table 1; the average values of k were calculated for the bimolecular approximation.

The results can be interpreted in terms of a mechanism involving synchronous proton and deuteron transfer in a cyclic intermediate with two H-bonds



It is interesting to compare the kinetic characteristics with the abilities of the functional groups to form H-bonds. The increasing proton-donor power in the series C_6H_5OH - p-ClC_6H_4OH (see, for example, Ref. /6/) is accompanied by an increasing rate of H-exchange with methanol. A similar dependence has been observed in the series of phenols /7/, alcohols and amines /5/ with mercaptan, alcohols with water /8/ and secondary amines with alcohols /4/. Ortho-chloro- and trichlorophenol are even stronger acids, but in these molecules there is intra-

Table 1

Kinetic parameters of the H-exchange processes studied

No.	ROH	$k_{20°C}$ l/mol sec	$k_{50°C}$ l/mol sec	E_a kcal/mol
1.	C_6H_5OH	240 ± 20	340 ± 20	2.1 ± 0.2
2.	p-ClC_6H_4OH	320 ± 30	440 ± 20	2.0 ±.0.2
3.	o-ClC_6H_4OH	65 ± 7	110 ± 10	3.3 ± 0.3
4.	2,4,6-$Cl_3C_6H_2OH$	37 ± 6	61 ± 6	3.1 ± 0.3

molecular H-bonding; in addition, o-chlorophenol is characterized by an equilibrium between cis and trans configurations. According to Ref. /6/, proton-acceptor substituents in ortho-position considerably decrease the association constants of phenols in intermolecular H-bonding. The H-exchange rate with methanol is considerably lowér in systems 3 and 4 (Table 1), than for phenol and p-chlorophenol; the decrease in k is accompanied by some increase in E_a. Such a decrease can be explaned by H-bonding of the hydroxyl proton with the Cl atom. This interaction hinders the formation of the intermediate, in which the proton is H-bonded to the alcohol oxygen.

A correlation between the rate and the proton donor ability of the molecule, as characterized by the energy of the H-bond or the pK_a value is always observed for reagents forming no intramolecular H-bonds /4, 5, 7, 8/. Intramolecular H-bonding in the molecules leads to the failure of this regularity.

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