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Kinetic Isotope Effect in Hydrogen Isotope Exchange Between Hydrogen Sulphide or Thiol and Alcohol in Gas and Solution

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The kinetic parameters of the tritium exchange between $H_2^*S(D_2^*S)$ or $MeSH^*(MeSD^*)$ and MeOH(MeOD) vapours on PTFE and glass surface were measured. The $^*HH/^*DD$ kinetic isotope effects are significantly lower than those for the reaction of phosphines with methanol. The kinetics of deuterium exchange between Bu^tSH and EtOD in solutions of C_6D_{12} and CD_3CN had been studied and HH/DD isotope effect was evaluated. It appeared to be smaller than that in the vapours. These results suggest that contrary to the exchange reactions in phosphine, the elementary reaction of HH-transfer in four center transition state is not the rate limiting step and H-bond formation as well as diffusion controlled processes should be taken into account.

Key words: kinetics, isotope, deuterium, exchange, isotope effect

Recently, the results of HH/DD kinetic isotope effect (KIE) between phosphines and methanol or water have been reported [1–3]. In above cases methanol and water could act as electron and proton donors, but phosphines act only as an electron donor. Hydrogen bonding with phosphines is considered to be very weak [4]. To complete our studies we choose the system, where both reagents have proton – donor and proton – acceptor abilities. In mixtures of alcohol with hydrogen sulphide (thiol), OH and SH groups act simultaneously as acceptor and donor of protons – this interaction leads to much stronger hydrogen bonding than in the previous cases, where phosphine – thiol and thiol – sulphide systems were studied [5,6]. The question arises how the replacement of phosphine for thiol changes the rate of exchange and how this change affects HH/DD KIE. For this purpose the tritium exchange between gaseous H_2S or MeSH and MeOH, and deuterium exchange between Bu^tSH and EtOH (in solution) were undertaken.

EXPERIMENTAL

a) The tritium exchange was studied in two parallel reactions:

$$H_2^*S(v)[MeSH^*(v)] + MeOH(v) = H_2S(v)[MeSH(v)] + MeOH^*(v) \qquad (1)$$

$$D_2^*S(v)[MeSD^*(v)] + MeOD(v) = D_2S(v)[MeSD(v)] + MeOD^*(v) \qquad (2)$$

Tritium specific radioactivities of H_2^*S, D_2^*S (94%D), $MeSH^*$ and $MeSD^*$ were 4.4×10^6, 6.2×10^6, 6.5×10^6 and 6.8×10^6 Bq/mol, respectively. The exchange was carried out: 1) in PTFE reactor and 2) in the glass reactor. The preparation of the PTFE and glass surfaces before the experiment, the separation of the gaseous reaction mixture and method of $H_2^*S(MeSH^*)$ radioactivity detection were described earlier [3,7,8].

b) The deuterium exchange reaction:

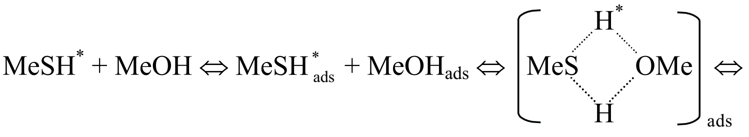
$$Bu^tSH + EtOD = Bu^tSD + EtOH \qquad (3)$$

was studied in C_6D_{12} and CD_3CN solutions. In these experiments the mixtures of Bu^tSH containing 0–90% of S-deuterated Bu^tSD and O-deuterated EtOD were used. The concentration of reagents was 0.05–0.1 mol/dm^3. The exchange fraction was evaluated from the integral of SH signal at 1.74 ppm and OH signal at 2.58 ppm. HMDS was used as the internal reference. The NMR tubes were successively filled with EtOD, $C_6D_{12}(CD_3CN)$, HMDS, Bu^tSD and Bu^tSH. The measurements of integrals of SH and OH started within 1 min after mixing of the substances in the NMR tube. The measurements were done with JEOL Co FX 90Q spectrometer equipped with a temperature probe. C_6D_6 served as the external lock. The spectra were recorded by using spectral width SW = 4000 Hz, the acquisition time AT = 2s and repetition number equal to 8.

The exchange fraction (F) was calculated from the equation:
$F = [I_t^{SH}(A_t^{SH}) - I_o^{SH}(A_o^{SH})]/[I_\infty^{SH}(A_\infty^{SH}) - I_o^{SH}(A_o^{SH})]$, where I^{SH} denotes integral of SH signal and A^{SH} denotes tritium radioactivity of $H_2S(MeOH)$. Subscripts o, t and ∞ refer to time t = 0, t, and time when the isotope equilibrium was reached, respectively.

RESULTS AND DISCUSSION

The kinetics of the reactions (1)–(3) could be described by McKay equation: $-\ln(1 - F) = kt$, where k is the exchange coefficient. The values of $k^{HH(DD)}$ for the reaction (1)–(2) are collected in Table 1. Additionally, the influence of PTFE surface on k was observed. If the ratio of S/V increases 2.2 times, k increases 1.5 times. Hence, we suppose that the exchange may run on the surface according to the mechanism shown in Scheme (4).



$$MeSH^* + MeOH \Leftrightarrow MeSH^*_{ads} + MeOH_{ads} \Leftrightarrow \left[MeS \; \overset{H^*}{\underset{H}{\diamond}} \; OMe \right]_{ads} \Leftrightarrow$$

$$\Leftrightarrow MeSH_{ads} + MeOH^*_{ads} \Leftrightarrow MeSH + MeOH^* \qquad (4)$$

The rate of exchange between $H_2S(MeSH)$ and MeOH is 10^2 times greater than that between Me_2PH and MeOH [2]. E_a for the reactions (1) – (2) are smaller than E_a for the reaction of alcohols with phosphines [1–3]. If we take into account that the rate coefficient for one H atom in H_2S is equal to $k^{HH}(k^{DD})/2$, we can conclude that the rate exchange in H_2S-MeOH and MeSH-MeOH mixtures is the same. The exchange between H_2S and MeOH on the glass surface goes 3 times faster than on the PTFE one. This finding may imply a stronger adsorption of reactants and a greater coverage of the glass surface than of the PTFE.

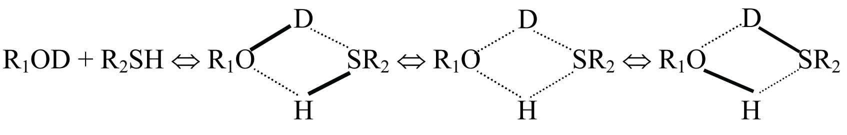
The KIE for H_2S-MeOH is close to that for MeSH-MeOH, however it is 2.5 times smaller than in the case of Me_2PH-MeOH (5.6 at 298 K) [2]. KIE equal to 2.2 (at 293 K) is too small to be related with the double HH/DD transfer in the transition complex (t.c.) like it was done in the case of phosphines [1–3], hence HH/DD transfer in t.c. cannot be the rate limiting step. As a result we suppose that in the present case the overall rate of the exchange reaction is determined by the rate of adsorption and/or the rate of H-bond formation.

Table 1. The k coefficients and KIE of heterogeneous tritium exchange in hydrogen sulphide-methanol and methanethiol-methanol vapour mixtures.

System	T [K]	10^2k^{HH} [s^{-1}]	10^2k^{DD} [s^{-1}]	k^{HH}/k^{DD}
H_2^*S(v)–MeOH(v)	293	6.08	3.06	2.0 ± 0.2
–glass [a)]	315	7.60	4.11	1.8 ± 0.1
	340	11.3	6.65	1.7 ± 0.1
	361	16.8	10.2	1.7 ± 0.15
	E_a^{HH} = 13.0 kJ/mol	E_a^{DD} = 15.4 kJ/mol	$E_a^{DD} - E_a^{HH}$ = 2.4 kJ/mol	
H_2^*S(v)–MeOH(v)	293	1.58	0.718	2.2 ± 0.15
–PTFE surface [b)]	315	2.62	1.25	2.1 ± 0.2
	340	3.77	1.79	2.1 ± 0.15
	361	5.42	2.85	1.9 ± 0.1
	E_a^{HH} = 15.5 kJ/mol	E_a^{DD} = 17.0 kJ/mol	$E_a^{DD} - E_a^{HH}$ = 1.5 kJ/mol	
$MeSH^*$(v)–MeOH(v)	293	0.718	0.342	2.1 ± 0.2
–PTFE surface [c)]	315	1.25	0.595	2.1 ± 0.15
	340	1.98	1.04	1.9 ± 0.2
	361	2.80	1.63	1.7 ± 0.15
	E_a^{HH} = 17.5 kJ/mol	E_a^{DD} = 20.0 kJ/mol	$E_a^{DD} - E_a^{HH}$ = 2.5 kJ/mol	

[a),b)] $P_{HSH} = P_{DSD} = 52$ hPa, $P_{MeOH} = P_{MeOD} = 40$ hPa; [c)] $P_{MeSH} = P_{MeSD} = 50$ hPa, $P_{MeOH} = P_{MeOD} = 44$ hPa.

KIE in the exchange between H_2S and MeOH on the glass surface is only slightly smaller than that observed on PTFE surface. Although the solvation – certainly existing on the glass – could decrease the KIE, this difference is too small (it does not exceed the estimated experimental error) to show any influence on KIE. The D-isotope exchange between EtOD and Bu^tSH in C_6D_{12} solution runs according to bimolecular mechanism. The total order of reaction equal to 1.8 and partial order referring to EtOH equal to 0.8 were measured. The results of kinetic measurements are collected in Table 2. In analogy to the exchange mechanism proposed earlier by Denisov [10] for the deuterium exchange between alcohols and thiols in CCl_4 solution (which goes *via* stable cyclic dimer with two H-bonds), we accept a similar reaction scheme for exchange between ethyl alcohol and butyl thiol in both our solutions:



⇔ $R_1OH + R_2SD$

R_1 = ethyl; R_2 = butyl.

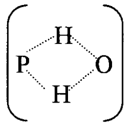
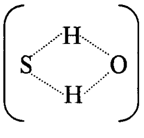
Table 2. The $k^{HH(DD)}$ coefficients, the bimolecular rate constants $k_b^{HH(DD)}$ and KIE of homogeneous deuterium exchange between t-butylthiol and ethanol in solutions.

Solvent	T [K]	10^3k^{HH} [s^{-1}]	10^3k^{DD} [s^{-1}]	$10^3k_b^{HH}$ [$dm^3mol^{-1}s^{-1}$]	$10^3k_b^{DD}$ [$dm^3mol^{-1}s^{-1}$]	k^{HH}/k^{DD}
C_6D_{12}	293	10.7	7.7	1.41	1.01	1.4 ± 0.2
CD_3CN	253	4.0	3.4	0.53	0.45	1.2 ± 0.2
	273	5.8	4.3	0.76	0.56	1.4 ± 0.2
	293	8.5	6.4	1.3	1.12	1.3 ± 0.15

The samples contain 5 μl (Bu^{t}SH + Bu^{t}SD) and 5 μl EtOD dissolved in 1 ml C_6D_{12}(CD_3CN).

Accepting this general scheme, we have to answer a more fundamental question – what is the rate determining step. In the acetonitrile solution the strong interaction between alcohol and acetonitrile (H-bonding and very strong dipole-dipole interaction) suggests that H(D) atom motions in cyclic dimer are coupled with CD_3CN molecules. This strong coupling should change not only the exchange rate in comparison to C_6D_{12} solution but should affect the KIE [9] as well. We observe quite different picture – the exchange rate in C_6D_{12} is only slightly higher than that in CD_3CN and we do not observe any visible change of KIE on the transfer from one solvent to the other. Above findings mean that HH(DD) double transfer elementary process is not the rate determining step. The small value of the KIE (1.4 at 293 K) suggests that the exchange rate is determined by the diffusion controlled processes rather than by any chemical process. The relative independence of KIE of temperature confirms this suggestion. It is worth to note that the results obtained do not exclude different specific mechanisms in both solvents (decoupled in C_6D_{12} and coupled in CD_3CN) because we claim that rearrangements in t.c. are not the slowest step of the reactions studied. It is then seen that the much smaller KIE in the solution is the immediate consequence of the existence of different processes determining the reaction rate in both cases.

The comparison of the results obtained presently with those for phosphine–alcohols system shows the substantial difference in the exchange mechanism between both cases. While in the previous case the double proton transfer in the transition complex was the rate determining step, presently other processes like diffusion, adsorption or complex formation are responsible for the exchange rate. It means that the elementary reaction (proton transfer) is much slower

in  complex than in  one.

This conclusion is in agreement with the previous observations [10,11], which have shown that the rate of hydrogen isotope exchange depends visibly on the strength of the hydrogen bonds in the transition complex – the stronger the hydrogen bonds the faster the exchange rate.

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