Kinetics of Deuterium Isotope Exchange between 2-Methylpropane-2-thiol and Propane-2-thiol in Aprotic Solvents

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The rate constants for bimolecular deuterium isotope exchange between 2-methylpropane-2-thiol and propane-2-thiol in C_6D_{12}, CCl_4, $(CD_3)_2CO$, $HCON(CH_3)_2$, $(CD_2)_4O$, and $(CH_3)_2SO$ solutions were determined by use of ^1H n.m.r. analysis. The rate constants, k, and activation enthalpy, $\Delta H^\ddagger$, decrease, and entropy, $-\Delta S^\ddagger$, increases, with an increase in the ability of the solvents to form hydrogen bonds with alkanethiols. The rate constant of concerted hydrogen transfer inside the cyclic dimer of alkanethiols with two H-bonds, k_3, increases with increasing dielectric constant of the solvent.

It has been shown that deuterium isotope exchange between alkanethiols in dilute cyclohexane solutions occurs according to a bimolecular mechanism.[1] The rate of isotope exchange in non-polar solvents (C_6D_{12}) depends on the formation constant of the mixed cyclic dimer with two H-bonds and on the rate constant of concerted H-transfer inside this dimer.[1,2] H-Transfer inside the cyclic complex is the slowest step.[1] The value of the formation constant of the cyclic dimer depends on the energies of the H-bonds. The mechanism of deuterium exchange between alkanethiols in aprotic non-polar and polar solvents capable of forming H-bonds is the subject of the present study. The basic question which arises is how concerted H-transfer inside the cyclic dimer is influenced by the presence of a polar solvent. The dielectric constant was chosen as a measure of solvent polarity.

Experimental

Kinetic Measurements.—The kinetics of deuterium isotope exchange between 2-methylpropane-2-thiol and propane-2-thiol in cyclohexane, carbon tetrachloride, acetone, tetrahydrofuran, dimethylformamide, and dimethyl sulphoxide were examined. Deuterium exchange between the alkanethiols and the solvents was not observed. 2-Methylpropane-2-thiol was a mixture of 40% perdeuteriated Bu^tSD and 60% non-deuteriated Bu^tSH. Propane-2-thiol was not deuteriated at the SH group. The solutions were prepared from freshly dehydrated alkanethiols and solvents in a dry nitrogen atmosphere.

N.m.r. tubes were successively filled with 2-methylpropane-2-thiol, solvent, propane-2-thiol, and TMS (internal reference) using microsyringes. The measurements were begun within 1 min of mixing the substances in the n.m.r. tube. All samples were run on a Tesla BS 487 C spectrometer operating at 80 MHz and equipped with a variable-temperature probe.

The SH signals of 2-methylpropane-2-thiol (1.75 p.p.m.) and propane-2-thiol (1.58 p.p.m.) could be observed separately in the spectrum of the reaction mixture. The increase in the intensity of the SH signal of 2-methyl-2-propanethiol during the exchange time was followed by integration.

Since the strong signal of cyclohexane at 1.43 p.p.m. was too close to that of the SH signal of Bu^tSH to be integrated properly, perdeuteriocyclohexane was used instead. Similar problems arose with acetone and tetrahydrofuran, and so the corresponding fully deuteriated solvents were used.

$$r = \frac{-\ln(1-F)}{t} \times \frac{n_1 n_2}{n_1 + n_2} \qquad (1)$$

Deuterium exchange follows the McKay law. The exchange rate, r, was evaluated from equation (1) where n_1, n_2 denote the concentrations of alkanethiols in mol dm^{-3}, F is the exchange fraction calculated from equation (2), and I_0^{SH}, I_t^{SH}, and I_∞^{SH} are the integral intensities of the SH signal of 2-methylpropane-2-thiol: initial, after time t, and at isotope equilibrium, respectively.

$$F = \frac{I_t^{SH} - I_0^{SH}}{I_\infty^{SH} - I_0^{SH}} \qquad (2)$$

Thermodynamic Measurements.—Equilibrium constants K, *i.e.* $1/K_1$ for complex formation between alkanethiol and the solvent, were established in separate experiments. The expression (3) was applied in a computer program. The concentration of alkanethiol was <0.5 mol dm^{-3} to avoid self-association, and the dilution of thiol in CCl_4 gave the value of the chemical shift of the thiol's monomer, δ_A.[3] The dependence of the chemical shift of the SH group, δ_{obs}, on the concentration of the solvent, B_0, was measured, and for a set of data pairs B_0—δ_{obs}, the equilibrium constant $1/K_1$ and the chemical shift of the SH group in the complex δ_{AB} have been obtained after an iteration sequence in a least-squares best fit analysis.

$$\frac{\delta_{obs} - \delta_A}{B_0} = -K(\delta_{obs} - \delta_A) + K(\delta_{AB} - \delta_A) \qquad (3)$$

Results and Discussion

The kinetics of deuterium exchange were studied over the temperature range 253—323 K in five solvents. The concentration of alkanethiols was from 0.1—2.0 mol dm^{-3}. The partial orders referring to 2-methylpropane-2-thiol are 0.9 ± 0.1, 0.9 ± 0.2, and 1.0 ± 0.2 in C_6D_{12}, $(CD_3)_2CO$, and $(CH_3)_2SO$, respectively. The partial orders referring to propane-2-thiol are 1.0 ± 0.2, 0.8 ± 0.1, and 1.1 ± 0.2 in C_6D_{12}, $(CD_3)_2CO$, and $(CH_3)_2SO$, respectively.

The above results show that deuterium exchange between alkanethiols occurs according to a bimolecular mechanism in both non-polar (cyclohexane) and polar (acetone, dimethyl sulphoxide) solvents. Hence, the rate constant, k, was calculated from equation (4).

$$r = k n_1 n_2 \qquad (4)$$

Table 1. The rate constants k at 303 K and activation parameters E_A, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for the isotopic exchange between 2-methylpropane-2-thiol and propane-2-thiol in various solvents

Solvent	$10^4 k$ at 303 K ($dm^3 mol^{-1} s^{-1}$)	E_A ($kJ mol^{-1}$)	$\Delta H^{\ddagger}$ ($kJ mol^{-1}$)	$-\Delta S^{\ddagger}$ ($J mol^{-1} K^{-1}$)
	1.7 ± 0.2			
C_6D_{12}	4.5 ± 0.3	27.0 ± 2.0	24.5 ± 2.0	228 ± 14
CCl_4	4.1 ± 0.2			
$(CH_3)_2S$	1.8 ± 0.15	31.0 ± 1.5	28.5 ± 1.5	222 ± 12
$(CD_3)_2CO$	1.4 ± 0.1	30.3 ± 2.0	27.7 ± 2.0	227 ± 15
$(CD_2)_4O$	1.0 ± 0.15	29.6 ± 1.5	27.1 ± 1.5	232 ± 12
$HCON(CH_3)_2$	1.2 ± 0.1			
$(CH_3)_2SO$	0.6 ± 0.08	28.7 ± 1.5	26.2 ± 1.5	239 ± 14

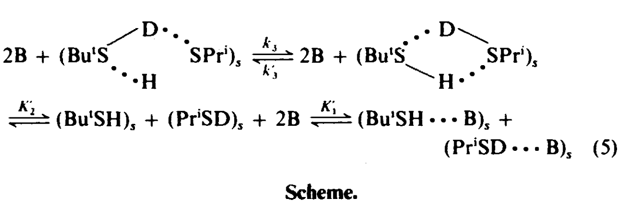
Table 2. Dimerization constants $1/K_1$, thermodynamic parameters $-\Delta H_1$, $-\Delta S_1$ for the interaction alkanethiol–solvent, and the ratios k/K_1 for the isotopic exchange in various solvents

Solvent		Pr^iSH			Bu^tSH			$10^6 k/K_1$ (s^{-1})	
	ε	$10^2 1/K_1$ at 303 K ($dm^3 mol^{-1}$)	$-\Delta H_1$ ($kJ mol^{-1}$)	$-\Delta S_1$ ($J mol^{-1} K^{-1}$)	$10^2 1/K_1$ at 303 K ($dm^3 mol^{-1}$)	$-\Delta H_1$ ($kJ mol^{-1}$)	$-\Delta S_1$ ($J mol^{-1} K^{-1}$)	Pr^iSH	Bu^tSH
$(CH_3)_2S$	6.2	3.0[a]	3.8	42	3.0	3.4	40	5.4	5.4
		2.8	3.7	41					
$(CH_3)_2CO$	20.7	4.7[a]	3.8	38	6.4[a]	3.8	35	6.6	9.0
$(CH_2)_4O$ $(CD_2)_4O$	7.4	6.1[a]	4.2	38	7.4	3.8	34	6.1	7.4
$HCON(CH_3)_2$	36.7	10	4.4	33	8.5[a]	3.8	33	12.0	10.1
$(CH_3)_2SO$	46.6	28	4.6	26	26	4.0	24	16.8	15.6

[a] See ref. 4.

The values of k at 303 K are presented in Table 1. These values are constant in the solvents used in the studied region of concentration of alkanethiols. However, the value of k in the two-component system of alkanethiols (*i.e.* without solvent) is about 3 times lower than that in the three component system with non-polar solvents (C_6D_{12}, CCl_4). This observation can be explained by the mutual solvation of alkanethiol molecules in the two-component system. The values of k decrease in the following order of solvents: C_6D_{12}, CCl_4, $(CH_3)_2S$, $(CD_3)_2CO$, $HCON(CH_3)_2$, $(CD_2)_4O$, and $(CH_3)_2SO$. Such a dependence agrees with an increase in the enthalpy of formation of an H-bond between alkanethiols and polar solvents (Table 2). The Arrhenius activation energies, E_A, calculated from the dependence of k on $1/T$, are presented in Table 1 for the solvents studied. It can be seen that E_A decreases with an increase in the ability of the solvent to form an H-bond with alkanethiols. The enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$, values are also presented in Table 1. The value of $-\Delta S^{\ddagger}$ increases with an increase in the enthalpy of formation of an H-bond between alkanethiols and solvents (Table 2).

It is assumed that an H-bond interaction of the type RSH ··· solvent (molar ratio 1:1) makes a significant contribution to the solvation of thiols by electron-donor solvents.[4,5] Hence, in this case, the D-exchange shown in the Scheme is proposed, where B denotes a solvent molecule participating in the formation of H-bonds with the thiol molecule, and s denotes the non-specific solvation of all forms of thiols.



Scheme.

It is assumed that H-isotope exchange between compounds with proton- and electron-donor XH and YH groups (X,Y = oxygen, nitrogen, sulphur, phosphorus) in the liquid and gas phases occurs *via* a cyclic H-bonded dimer.[1,2,6] The existence of cyclic dimers of thiols is confirmed by the results obtained from the autoassociation of RSH[3,7] and also by *ab initio* theoretical calculations.[8-10]

Applying a steady-state assumption to the Scheme, taking into account that concentrations of the cyclic dimer before and after exchange are constant, assuming further that concerted H-transfer inside the cyclic dimer is the slowest step,[1] and neglecting isotope effects ($K_1 = K_1'$, $K_2 = K_2'$, $k_3 = k_3'$), the expression (6) is obtained.[2]

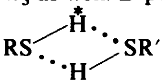
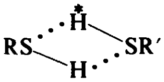
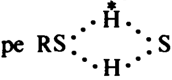
$$r = k_3K_1K_2n_1n_2 = k_3K_cn_1n_2 \tag{6}$$

In the above expression, k_3 is the rate constant of concerted H-transfer inside the cyclic dimer, K_1 is the dissociation constant of the H-bond between the thiol and solvent molecules, K_2 is the formation constant of the cyclic dimer from monomers of thiols, and K_c is the formation constant of the cyclic complex from thiols H-bonded to the solvent. The approximations that $K_1 = K_1'$ and $K_2 = K_2'$ are valid because the values of the dimerization constants for H-bond formation *via* protons and deuterons are similar for alkanethiols[11] and alcohols.[12] The measured value of the kinetic isotopic effect k_H/k_D at 303 K for the exchange between 2-methylpropane-2-thiol and propane-2-thiol,[5] in CCl_4, is equal to 2.6, *i.e.* relatively small, and the approximation $k_3 = k_3'$ can be made. The enthalpy ΔH_c is the difference between the heats of formation of the thiol monomers resulting either from the cyclic dimer (ΔH_2) or from the monomers H-bonded with the solvent ($-\Delta H_1$). The entropy ΔS_c is equal to $\Delta S_2 - (-\Delta S_1)$.

The equation $k = k_3K_1K_2$, obtained from expressions (4) and (6), deserves further consideration. The values of $1/K_1$ for the interaction between Bu^tSH or Pr^iSH and the electron-donor solvents applied in kinetic experiments were obtained in the temperature range 263—323 K, in CCl_4. The value $1/K_1$ at 303 K and $-\Delta H_1$, $-\Delta S_1$ for the above interaction are collected in Table 2. Some of the data presented in this Table were taken from S. I. Miller and co-workers.[4]

The dependence of k/K_1 on the type of solvent could be established. The values of k/K_1 (using $1/K_1$ referring to Bu^tSH and Pr^iSH) for various solvents are presented in the last column of Table 2. It can be seen that the value of k/K_1 (*i.e.* k_3K_2) increases with increasing dielectric constant (ε) of the solvent.

The value of $-\Delta H_2$, and also that of K_2, decreases with increasing ε.[6,13] This can be explained by the stronger non-specific solvation of thiol monomers relative to that of the cyclic dimer.[6]

Taking into account that the value of k_3K_2 increases while that of K_2 diminishes with the increase in ε one should expect an increase in k_3 as well. Dipole moments in the stable complexes of the type  and  are close to zero in non-polar solvents.[1] The hydrogen atoms in an activated complex of the type  (the transition state in reaction path of concerted H-transfer inside stable dimers[6]) are probably symmetrically localized[1] and the dipole moment in this dimer is also close to zero. The above conclusions result from the fact that the energies of the SH ··· S bonds in the complex of Bu^{t}SH with Pr^{i}SH are similar.[3] According to Kirkwood and Laidler's theory,[14] the dipole moments in the activated complex and in the stable dimers increase with increasing ε of the solvent. The increase in the rate constant k_3 with ε can be explained by the formation of the activated complex with a dipole moment larger that the dipole moments of stable dimers.[14] The changes in the dipole moments of transition and stable complexes cause the changes in solvation of the above dimers. These changes in solvation may introduce a significant contribution[15] to the energies of activation of H-transfer inside the dimer, E_3. The value of E_3 is the difference between the energies of the activated complex and the stable dimers.[6] Caldin and Mateo[15] suggest that the motions of the solvent molecules are coupled with the motions of protons in the more polar solvent. They have shown that the effective mass of the transferred hydrogen is significantly higher than 1.00 atomic units in the reaction between $NO_2C_6H_4CH_2$-NO_2 and $HN{=}C(NMe_2)_2$ in solvents such as tetrahydrofuran, methylene dichloride, and acetonitrile (these solvents have $\varepsilon > 7$). The coupling of the motions of the solvent molecules and protons induces the reorganization of the solvation sphere[15] in the dimer which, in turn, alters the entropy $\Delta S_3^‡$. This coupling is expected to reduce the value $\Delta H_3^‡$ but, on the other hand, it should decrease the tunneling probability as the effective mass for motion along the reaction co-ordinate increases.[15] However, it is not known which of the factors, either $\Delta H_3^‡$ or $\Delta S_3^‡$, influences the value of k_3, and further studies are required.

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