Kinetic Isotope Effect in Hydrogen Isotope Exchange between Diphenylphosphine and Methanol or 2-Methylpropane-2-thiol in Aprotic Solvents

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The bimolecular rate constants for tritium exchange between (i) Ph_2PH and $MeOH^*$, (ii) Ph_2PD and $MeOD^*$, (iii) Ph_2PH and Me_3CSH^*, and (iv) Ph_2PD and Me_3CSD^* in MeCN solution were measured. In systems (i) and (ii) the HT/DT kinetic isotope effect depends on the direction of exchange and varies from 3.0 to 1.7 and from 4.8 to 2.4 at 323 and 250 K, respectively. In systems (iii) and (iv) the kinetic isotope effect is independent of the direction of exchange and changes from 2.2 at 323 K to 2.8 at 250 K. The rate constants for deuterium exchange between Ph_2PH and MeOH or Me_3CSH were measured in C_6H_6, C_2Cl_4, $(CH_2)_4O$, C_5H_5N and MeCN solutions. The reactions involve (i) desolvation of MeOH or Me_3CSH (ii) double hydrogen transfer in the four-centre cyclic complex, which is found to be the rate limiting-step. The contribution of tunnelling to hydrogen transfer is not significant.

Hydrogen migration plays an important role in numerous biological processes but its mechanism is still not completely understood, especially in systems with PH and SH groups. The kinetics and kinetic isotope effects (KIEs) of non-catalysed hydrogen exchange have been widely studied in protic and aprotic media,[1-8] but there are few data which concern hydrogen exchange in thiols and phosphines.[8-10]

The aim of this study was to establish the mechanism of reaction, the rate-limiting step and the role of tunnelling in hydrogen isotope exchange between 2-methylpropane-2-thiol and diphenylphosphine and also between methanol and diphenylphosphine in aprotic solvents by means of the KIEs.

Experimental

Reagents.—2-Methylpropane-2-thiol (Me_3CSH) was from Fluka (reagent grade). The exchange in the SH group was carried out in six steps with 99.9% D_2O, and the Me_3CSD contained 97% deuterium. Tritium-labelled Me_3CSH^* and Me_3CSD^* (96% deuterium) were prepared by heterogenous exchange with HTO and HTO dissolved in D_2O. Methanol (MeOH; spectroscopy grade) and MeOD, 99.7% deuterium (IBJ–Świerk, Poland) were used. Tritium labelled alcohols were obtained by exchange with HTO and dehydration over molecular sieves. Diphenylphosphine (Ph_2PH) was from Aldrich (reagent grade). Ph_2PD, 96% deuterium, was obtained in five steps by homogenous exchange with 99.7%. MeOD. After each step the MeOD was distilled off under a high vacuum. The reagents and solvents were dehydrated over 3 Å molecular sieves.

Measurements of Deuterium Exchange.—In the kinetic studies NMR tubes were successively filled with 40% Ph_2PD/60% Ph_2PH, solvent, MeOH (Me_3CSH) and tetramethylsilane as an internal reference, using microsyringes. The measurements were started 1 min after mixing. The samples were run on a Tesla-487C spectrometer operating at 80 MHz and equipped with a variable-temperature probe. The PH signals of Ph_2PH [δ 4.12 and 6.82 (d)] and the SH signal of Me_3CSH (δ 2.08) or OH signal of MeOH could be observed separately.

The deuterium exchange fraction, F^{HD}, was calculated from equation (1). The D/H fractionation factor between Ph_2PH and MeOD (Me_3CSD), α^{HD}, was obtained from equation (2) which is derived from the isotope balance [equation (2)]. The exchange follows the McKay law, therefore the exchange rate, r^H, was calculated from equation (3). Here m_1 denotes the total concentration of MeOH (Me_3CSH), m_2 is the concentration of Ph_2PH and I_0^{PH}, I_t^{PH}, I_∞^{PH} are the initial integral intensity of the PH signal, the intensity after time t and the intensity at isotope equilibrium, respectively.

$$F^{HD} = (I_t^{PH} - I_0^{PH})/(I_\infty^{PH} - I_0^{PH}) \quad (1)$$

$$\alpha^{HD} = [m_2(I_\infty^{PH} - I_0^{PH})^2]/[I_\infty^{PH}(m_1 I_0^{PH} + m_2 I_\infty^{PH} - m_2 I_0^{PH})] \quad (2)$$

$$r^H = [-\ln(1 - F^{HD})/t][m_1 m_2/(m_1 + \alpha^{HD} m_2)] \quad (3)$$

Measurements of Tritium Exchange.—Tritium exchange took place in four thermostatted bulbs filled with (i) Ph_2PH, Me_3CSH^* and MeCN; (ii) Ph_2PD, Me_3CSD^* and MeCN; (iii) Ph_2PH, $MeOH^*$ and MeCN; and (iv) Ph_2PD, $MeOD^*$ and MeCN. Small amounts of the solutions were taken for analysis during the reaction. Me_3CSH (MeOH) was extracted from the acetonitrile to hexane. It was established that the molar ratio of Ph_2PH to MeOH (Me_3CSH) in the hexane phase was <0.02. The amounts of Me_3CSH^* Me_3CSD^*, $MeOH^*$ and $MeOD^*$ were determined by IR spectroscopy from the integral intensities of the bands due to SH, SD, OH and OD stretching vibrations. Small concentrations of thiol or methanol in the hexane were also determined by ^{13}C NMR spectroscopy. The spectra were recorded at 22.5 MHz on a JEOL Co FX 90Q spectrometer with a gated-decoupling technique to eliminate nuclear Overhauser enhancement effects. The total radioactivity of the samples was measured by the scintillation method; portions of n-hexane solutions with alcohol (thiol) were dissolved in the scintillator fluid [2,5-diphenyloxazole (PPO) and 1,4-bis-(5-phenyloxazol-2-yl)benzene (POPOP) in toluene] and the radioactivity was determined with a Beckman LS-7000 counter.

The tritium exchange fraction, F^{HT}, was evaluated from equation (4) and the *T*/*H* fractionation factor, α^{HT}, from

Table 1 Solvent effect on the activation parameters of deuterium isotopic exchange

System	Solvent	E_T[a]	ε	$k^{HD}/10^{-4}$ dm^3 mol^{-1} s^{-1} (303 K)[b]	E_a/kJ mol^{-1}
Ph_2PH–MeOH	C_6H_6	34.5	2.28	78.2	18.6
	C_2Cl_4	31.9	2.30	74.5	19.2
	$(CH_2)_4O$	37.4	7.1	64.1	19.4
	C_5H_5N	40.2	12.3	26.0	26.6
	MeCN	46.0	37.4	61.8	20.8
Ph_2PH–Me_3CSH	C_6H_6	34.5	2.28	1.85	43.0
	$(CH_2)_4O$	37.4	7.1	2.68	41.7
	C_5H_5N	40.2	12.3	3.45	40.3
	MeCN	46.0	37.4	5.07	38.1

[a] Ref. 33. [b] The relative error in k is less than 4%.

Table 2 Fractionation factors[a]

System	T/K	α^{HD}	α^{HT}	α^{DT}
Ph_2PH–MeOH	250	0.438	0.310	0.621
	273	0.462	0.333	0.641
	288		0.349	0.654
	303	0.501	0.365	0.662
	323		0.384	0.675
Ph_2PH–Me_3CSH	250		0.97	0.99
	273		0.97	0.98
	303	0.96	0.95	0.98
	323	0.95	0.93	0.97

[a] The relative error in α is less than 3%.

$$MeOT(C_4H_9ST) + Ph_2PH \underset{k^{HT}}{\overset{\alpha^{HT}k^{HT}}{\rightleftharpoons}} MeOH(C_4H_9SH) + Ph_2PT$$

$$MeOT(C_4H_9ST) + Ph_2PD \underset{k^{DT}}{\overset{\alpha^{DT}k^{DT}}{\rightleftharpoons}} MeOD(C_4H_9SD) + Ph_2PT$$

Scheme 1

$$F^{HT} = [A_0^{OH(SH)} - A_t^{OH(SH)}]/[A_0^{OH(SH)} - A_\infty^{OH(SH)}] \quad (4)$$

equation (5). The values of $A_0^{OH(SH)}$, $A_t^{OH(SH)}$, and

$$\alpha^{HT} = A_\infty^{PH}/A_\infty^{OH(SH)} \quad (5)$$

$A_\infty^{OH(SH)}$ denote tritium specific radioactivity of MeOH* (Me_3CSH*) at $t = 0$, t and ∞, respectively. The value of A_∞^{PH}, *i.e.* the specific radioactivity of Ph_2PH*, was obtained from the isotope balance in equation (6). The exchange fraction,

$$m_1A_0^{OH(SH)} = m_1A_\infty^{OH(SH)} + m_2A_\infty^{PH} \quad (6)$$

F^{DT}, and fractionation factor, α^{DT}, were obtained from equations (4) and (5) replacing the tritium specific radioactivities of MeOH*, Me_3CSH* and Ph_2PH* with those of MeOD*, Me_3CSD* and Ph_2PD*.

Results

Deuterium Exchange.—For the reaction of Ph_2PH with Me_3CSH at 303 K in benzene (B) and MeCN the partial orders with respect to Ph_2PH are 1.0 ± 0.2 (B) and 1.1 ± 0.2 (MeCN), and with respect to Me_3CSH are 1.0 ± 0.1 (B) and 1.2 ± 0.2 (MeCN). The partial orders for the reaction of Ph_2PH with MeOH at 263 K are 0.9 ± 0.2 (B) and 1.0 ± 0.1 (MeCN) with respect to Ph_2PH, and 1.1 ± 0.1 (B) and 0.9 ± 0.1 (MeCN) with respect to MeOH. Hence, both exchange reactions are bimolecular in the solvents studied, and the rate constant, k^{HD}, can be estimated from the equation: $r^H = k^{HD}m_1m_2$.

For the reaction between Ph_2PH and MeOH in tetrachloroethylene the values of k^{HD} were found to be independent of the concentration of MeOH below 1 mol dm^{-3}. In the concentration range 1.08–9.2 mol dm^{-3} the decrease in k^{HD} can be explained by the predominant self-association of MeOH.[11] In the case of exchange between Ph_2PH and Me_3CSH, dependence of k^{HD} on the concentration was not observed because Ph_2PH[12] and Me_3CSH[13,14] exist mainly as monomers in solution. Hence, the concentration of reagents for both systems in kinetic measurements was kept below 1 mol dm^{-3}.

The kinetic data for deuterium exchange in aprotic solvents are given in Table 1. For the system Ph_2PH–Me_3CSH the values of k^{HD} increase and of E_a decrease with increasing solvent polarity, whereas for the system Ph_2PH–MeOH the values of k^{HD} decrease and of E_a slightly increase (except in pyridine). Deuterium exchange in the system Ph_2PH–MeOH, at 303 K, is *ca.* 10–40 times faster than in the Ph_2PH–Me_3CSH system, and E_a is *ca.* 2.5 times greater for the latter system.

Kinetic Isotope Effects.—The tritium exchange proceeds *via* a bimolecular mechanism in two parallel reactions (Scheme 1). $\alpha^{HT}k^{HT}$ and $\alpha^{DT}k^{DT}$ are the rate constants for the forward process and k^{HT} and k^{DT} are the rate constants for the reverse process. k^{HT} and k^{DT} are given by equation (7). In order to

$$k^{HT(DT)} = -\ln[1 - F^{HT(DT)}]/[m_1 + \alpha^{HT(DT)}m_2]t \quad (7)$$

obtain k^{HT} and k^{DT} as well as $\alpha^{HT}k^{HT}$ and $\alpha^{DT}k^{DT}$, α^{HT} and α^{DT} must be known. The latter were measured over the range 250–323 K in acetonitrile solutions (Table 2). Using Bigeleisen–Swain relations,[15,16] *i.e.* $\ln \alpha^{HT} = (1.44 \pm 0.11) \ln \alpha^{HD}$ and $\ln \alpha^{DT} = (0.44 \pm 0.11) \ln \alpha^{HD}$, the values of α^{HT} and α^{DT} were calculated from α^{HD} data (Table 2). The experimentally obtained α^{HT} and α^{DT} agree with the calculated values and were used for the estimation of the rate constants from equation (7).

Plots of $-\ln(1 - F)$ *vs.* t for tritium exchange in the systems DPP–MA*, [$^2H_1$]DPP–[$^2H_1$]MA* and DPP–MPT*, [$^2H_1$]-DPP–[$^2H_1$]MPT* in MeCN are presented in Figs. 1 and 2. The values of the rate constants, activation energies, pre-exponential factors and kinetic isotope effects for both directions of exchange in the systems DPP–MA and DPP–MPT are given in Tables 3 and 4.

Discussion of Exchange Mechanism

Small changes in k^{HD} and E_a (Table 1) estimated in non-polar and polar solvents indicate that the solvent has a minor

Table 3 The rate constants, activation parameters and KIE for tritium exchange in the Ph_2PH–MeOH system[a]

T/K	$k^{HT}/10^{-3}$ dm^3 mol^{-1} s^{-1}	$k^{DT}/10^{-3}$ dm^3 mol^{-1} s^{-1}	k^{HT}/k^{DT}	$\alpha^{HT}k^{HT}/10^{-3}$ dm^3 mol^{-1} s^{-1}	$\alpha^{DT}k^{DT}/10^{-3}$ dm^3 mol^{-1} s^{-1}	$\alpha^{HT}k^{HT}/\alpha^{DT}k^{DT}$
250	1.86	0.387	4.8 ± 0.3	0.577	0.240	2.4 ± 0.15
273	4.06	0.890	4.6 ± 0.3	1.35	0.570	2.4 ± 0.15
288	5.95	1.48	4.0 ± 0.2	2.07	0.966	2.1 ± 0.1
303	8.10	2.37	3.4 ± 0.2	2.96	1.56	1.9 ± 0.1
323	13.0	4.36	3.0 ± 0.2	5.00	2.94	1.7 ± 0.1

Forward exchange

$E_a'^{HT} = 18.0 \pm 1.0$
$E_a'^{DT} = 22.0 \pm 1.1$
$E_a'^{DT} - E_a'^{HT} = 4.0$
$A'^{HT} = 10.6 \pm 4.6$
$A'^{DT} = 16.1 \pm 7.1$
$A'^{HT}/A'^{DT} = 0.66$

Reverse exchange

$E_a^{HT} = 19.9 \pm 0.8$
$E_a^{DT} = 22.7 \pm 1.2$
$E_a^{DT} - E_a^{HT} = 2.8$
$A^{HT} = 8.53 \pm 3.70$
$A^{DT} = 14.7 \pm 5.3$
$A^{HT}/A^{DT} = 0.58$

[a] E_a are in kJ mol^{-1}; A are in dm^3 mol^{-1} s^{-1}; the relative error in k is less than 3%.

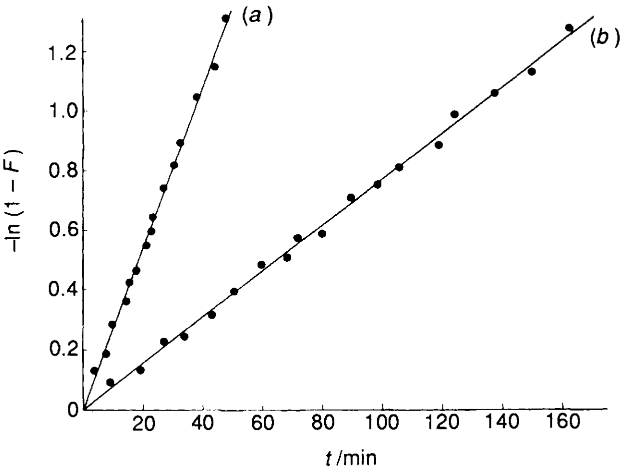

Fig. 1 Plots of $-\ln(1 - F^{HT(DT)})$ vs. t at 250 K: (a) for MeOH*–Ph_2PH ([MeOH] = 0.175 mol dm^{-3}; [Ph_2PH] = 0.210 mol dm^{-3}); (b) for MeOD*–Ph_2PD ([MeOD] = 0.191 mol dm^{-3}; [Ph_2PD] = 0.227 mol dm^{-3})

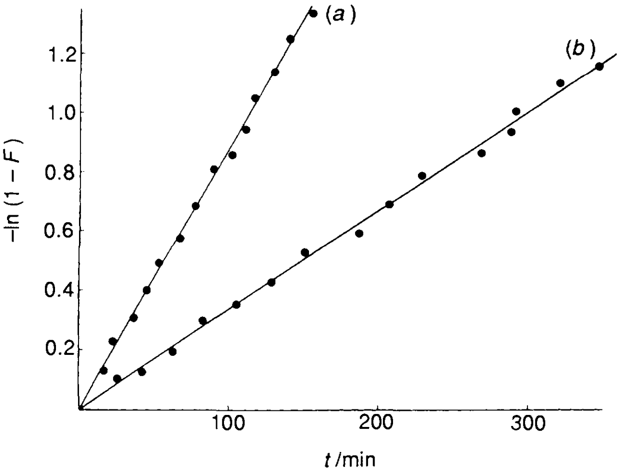

Fig. 2 Plots of $-\ln(1 - F^{HT(DT)})$ vs. t at 273 K: (a) for Me_3CSH*–Ph_2PH ([Me_3CSH] = 0.711 mol dm^{-3}; [Ph_2PH] = 0.732 mol dm^{-3}); (b) for Me_3CSD*–Ph_2PD ([Me_3CSD] = 0.728 mol dm^{-3}; [Ph_2PD] = 0.750 mol dm^{-3})

influence on the rate-limiting step and therefore on the exchange mechanism.

Thiols and alcohols have proton donor and/or electron donor properties,[11,13,14] and Ph_2PH acts as an electron donor.[17] The ability of Ph_2PH to form hydrogen bonds is a subject of some controversy. The PH-group stretching frequency shift, *ca.* 15 cm^{-1}, in the self-association of disubstituted phosphine oxides or phosphine sulphides[18] suggests that a very weak PH ··· X bond can be formed. The downfield ^{1}H NMR shift of the PH group signal, *ca.* δ 0.05 ppm, on increasing the concentration of diethyl sulphide or tributylphosphine,[12] conforms this suggestion. However, a ^{31}P and ^{1}H NMR study on the self-association of Ph_2PH in C_6D_6[19] and an *ab initio* calculation[20] exclude the possibility of PH ··· X bond formation. In conclusion, the formation of the stable cyclic dimer $\mathrm{O(S)}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\cdots\quad\cdots}}\mathrm{P}$ is unlikely because the energies of the O(S)H ··· P[11,17] and PH ··· O(S)[12,18] bonds differ too much. Hence, a two-step mechanism involving (i) the formation of a stable cyclic dimer and (ii) synchronous hydrogen transfer within the dimer,[8,9] is excluded.

All isotopic structures of the ion pair for the reaction in Scheme 1 are shown in Fig. 3. The arrows assign the jump of hydrogen atoms from the less to the more electron-donating heavy atoms and the wavy lines assign the rupture of the bond in the reverse hydrogen transfer. The bond rupture is the rate-limiting step because E_a for the formation of the ion pair is smaller than for the reverse process.[8] Hence, the H/D KIE should be primary for reactions occurring *via* the structures (**a**) and (**b**) and secondary for reactions involving the structures (**c**) and (**d**). The maximum value of the secondary H/D KIE is 1.4 at 293 K.[24] Experimental values of KIE are significantly greater than 1.4. Hence, the exchange mechanism involving an ion pair is also excluded.

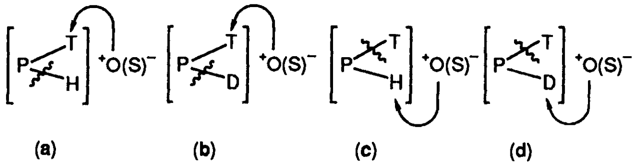

Fig. 3

It is proposed that the exchange occurs directly *via* a four-centre transition state $\mathrm{O(S)}\begin{smallmatrix}\cdot\cdot\,\mathrm{H}\,\cdot\cdot\\ \cdot\cdot\,\mathrm{H}\,\cdot\cdot\end{smallmatrix}\mathrm{P}$. Non-linear three-centre transition states for a single hydrogen transfer in the hydride ion,[21,22,23] and cyclic transition states for a double hydrogen transfer in a MeOH–$MeCO_2H$ mixture, have been

Table 4 The rate constants, activation parameters and KIE for tritium exchange in the Ph_2PH–Me_3CSH system[a]

T/K	$k^{HT}/10^{-5}$ dm^3 mol^{-1} s^{-1}	$k^{DT}/10^{-5}$ dm^3 mol^{-1} s^{-1}	k^{HT}/k^{DT}	$\alpha^{HT}k^{HT}/10^{-5}$ dm^3 mol^{-1} s^{-1}	$\alpha^{DT}k^{DT}/10^{-5}$ dm^3 mol^{-1} s^{-1}	$\alpha^{HT}k^{HT}/\alpha^{DT}k^{DT}$
250	2.55	0.897	2.8 ± 0.2	2.63	0.910	2.9 ± 0.2
273	10.7	3.88	2.7 ± 0.15	11.0	3.92	2.8 ± 0.2
303	40.9	17.0	2.4 ± 0.2	43.5	17.7	2.5 ± 0.2
323	96.7	43.8	2.2 ± 0.15	104	45.2	2.3 ± 0.15

Forward exchange

$E_a'^{HT} = 33.3 \pm 0.6$
$E_a'^{DT} = 35.6 \pm 0.7$
$E_a'^{DT} - E_a'^{HT} = 2.3$
$A'^{HT} = 244 \pm 65$
$A'^{DT} = 261 \pm 82$
$A'^{HT}/A'^{DT} = 0.93$

Reverse exchange

$E_a^{HT} = 33.7 \pm 0.6$
$E_a^{DT} = 35.9 \pm 0.7$
$E_a^{DT} - E_a^{HT} = 2.2$
$A^{HT} = 306 \pm 70$
$A^{DT} = 291 \pm 88$
$A^{HT}/A^{DT} = 1.05$

[a] E_a are in kJ mol^{-1}; A are in dm^3 mol^{-1} s^{-1}; the relative error in k is less than 4%.

$$(MeOT)C_4H_9ST\cdots S + Ph_2PH \underset{k_2^{HT}}{\overset{k_1^{HT}}{\rightleftharpoons}} (MeOT)C_4H_9ST + Ph_2PH + S \underset{k_3'^{HT}}{\overset{k_3^{HT}}{\rightleftharpoons}} (MeOH)C_4H_9SH + Ph_2PT + S \underset{k_1'^{HT}}{\overset{k_2'^{HT}}{\rightleftharpoons}} (MeOH)C_4H_9SH\cdots S + Ph_2PT$$

$$(MeOT)C_4H_9ST\cdots S + Ph_2PD \underset{k_2^{DT}}{\overset{k_1^{DT}}{\rightleftharpoons}} (MeOT)C_4H_9ST + Ph_2PD + S \underset{k_3'^{DT}}{\overset{k_3^{DT}}{\rightleftharpoons}} (MeOD)C_4H_9SD + Ph_2PT + S \underset{k_1'^{DT}}{\overset{k_2'^{DT}}{\rightleftharpoons}} (MeOD)C_4H_9SD\cdots S + Ph_2PT$$

Scheme 2

reported.[7] In addition, *ab initio* calculations have shown that the cyclic dimers of H_2O or NH_3 are the preferred transition states in hydrogen rearrangement.[20]

The assumed reaction path for tritium exchange in the presence of the solvent, S, is given in Scheme 2, where $k_1 (k'_1)$ is the rate constant for the decomposition of the hydrogen bonded complex, k_2 (k'_2) is the rate constant for the formation of this complex, and k_3 (k'_3) is the rate constant for the hydrogen transfer.

The T/H (T/D) equilibrium isotope effect of hydrogen bond formation between solvent and MeOH or Me_3CSH (Scheme 2) should be close to unity.[25,26] The T/H (T/D) KIE of hydrogen bond formation differs from unity by *ca.* 1%, assuming that this effect depends only on the diffusion rate of the isotopic species, *i.e.* on the square root of the total mass of these species. Hence, the T/H (T/D) KIE for hydrogen bond dissociation can differ from unity by only a few per cent.[25,26] Thus the exchange *via* a four-centre transition state, rather than desolvation or solvation, is the most likely rate-limiting step as indicated by the large measured value of the KIE.

Considering the values of the rate constants in Schemes 1 and 2, and taking into account that hydrogen isotope transfer is the rate limiting step, equations (8a) and (8b) are obtained, where

$$k^{HT}/k^{DT} = (K_1'^{HT}/K_1'^{DT}) \times (k_3'^{HT}/k_3'^{DT}) \qquad (8a)$$

$$\alpha^{HT}k^{HT}/\alpha^{DT}k^{DT} = (K_1^{HT}/K_1^{DT}) \times (k_3^{HT}/k_3^{DT}) \qquad (8b)$$

$K_1^{HT}/K_1^{DT} = (k_1^{HT}/k_1^{DT})/(k_2^{HT}/k_2^{DT})$ and is equal to unity, whereas $K_1'^{HT}/K_1'^{DT} = (k_1'^{HT}/k_1'^{DT})/(k_2'^{HT}/k_2'^{DT}) \neq 1$ (Scheme 2). The value of $k_3'^{HT}/k_3'^{DT}$ was obtained from equation (8a). The values of k_3^{HT}/k_3^{DT} are the same as those of $\alpha^{HT}k^{HT}/\alpha^{DT}k^{DT}$ [equation (8b)]. The equilibrium isotope effects for desolvation and KIEs for hydrogen transfer at 303 K for both systems are listed in Table 5.

The Bell criteria of tunnelling,[1,2] *i.e.* the maximum values of k_3^H/k_3^D, $E_{a3}^D - E_{a3}^H$ and values A^H/A^D predicted by semiclassical theory for the three-centre linear complex, were used for the four centre cyclic complex. For the transition states $O(S)\underset{\cdot\cdot H\cdot\cdot}{\overset{\cdot\cdot T\cdot\cdot}{\vdots\quad\vdots}}P$ and $O(S)\underset{\cdot\cdot D\cdot\cdot}{\overset{\cdot\cdot T\cdot\cdot}{\vdots\quad\vdots}}P$ the zero-point energy is associated only with OH(PH) and OD(PD) or SH(PH) and SD(PD) stretching frequencies and is lost in such a transition state. It has been proved that the Bell criteria are fulfilled in the case of the double hydrogen transfer in the cyclic complex of methanol and acetic acid.[7] The maximum semiclassical values of k_3^{HT}/k_3^{DT} and $E_{a3}^{DT} - E_{a3}^{HT}$ for the systems studied are listed in Table 5. The values of k_3^{HT}/k_3^{DT} ($k_3'^{HT}/k_3'^{DT}$) and $E_{a3}^{HT} - E_{a3}^{HT}$ ($E_{a3}'^{DT} - E_{a3}'^{HT}$) are smaller than those predicted by semiclassical theory, therefore the contribution of tunnelling in hydrogen transfer should be small. This is confirmed by the experimental values of A^H/A^D in the region 0.58–1.05 (Tables 4 and 5).[1,2]

The influence of solvent polarity on hydrogen transfer should also be considered. The values of k_3 are estimated from the equation $k_3 = k^{HD}/K_1$ and are presented in Table 6, with the dimerization constants, $1/K_1$, and thermodynamic parameters, ΔH_1, for the interaction of MeOH and Me_3CSH with various solvents. It is noteworthy that k_3 increases and $\Delta H_3^{\ddagger}$ decreases with increasing polarity, expressed as ε and E_T, of the solvents. This can be explained by taking into account the suggestion of Caldin[3] that the motions of solvent molecules are coupled with the motions of hydrogen atoms. Such coupling is expected to reduce the value of $\Delta H_3^{\ddagger}$. The coupling should decrease the probability of tunnelling since the effective mass for motion along the reaction co-ordinate increases.[3] Indeed, the contribution of tunnelling to the exchange reaction in acetonitrile was small.

Conclusions

KIEs were measured using all three hydrogen isotopes. The

Table 5 Isotope effects for desolvation and hydrogen transfer

System	$K'_1{}^{HT}/K'_1{}^{DT}$	$k'_3{}^{HT}/k'_3{}^{DT}$ (303 K)	$(\Delta H'_1{}^{DT} - \Delta H'_1{}^{HT})$ /kJ mol^{-1}	$(E'_{a3}{}^{DT} - E'_{a3}{}^{HT})$ /kJ mol^{-1}	$k_3{}^{HT}/k_3{}^{DT}$ (303 K)	$(E_{a3}{}^{DT} - E_{a3}{}^{HT})$ /kJ mol^{-1}
Experimental values						
Ph_2PH–MeOH	1.12[a]	3.0	0.8[a]	3.2	1.9	2.8
Ph_2PH–Me_3CSH	1.06[b]	2.3	−0.6[b]	2.9	2.5	2.2
Maximum semiclassical values						
Ph_2PH–MeOH	—	7.9[c]	—	5.10[c]	4.2[e]	3.55[e]
Ph_2PH–Me_3CSH	—	4.9[d]	—	3.89[d]	4.2[e]	3.55[e]

[a] For the decomposition of the dimer of MeOH and MeOD at 293 K from ref. 25. [b] For the decomposition of the dimer of MeSH and MeSD at 308 K from ref. 26. [c] For OH and OD bonds at 298 K from ref. 2. [d] For SH and SD bonds at 298 K from ref. 2. [e] For PH and PD bonds at 298 K calculated from stretching frequencies.

Table 6 Dimerization constants $1/K_1$ at 303 K and ΔH_1 for the interaction of MeOH and Me_3CSH with the solvent in comparison with the rate constants k_3 at 303 K and $\Delta H_3^{\ddagger}$ for deuterium exchange

Compound	Solvent	$(1/K_1$/mol dm^{-3}	$-\Delta H_1$/kJ mol^{-1}	$k_3/10^{-5}$ s^{-1}	$\Delta H_3^{\ddagger}$/kJ mol^{-1}
MeOH	$(CH_2)_4O$	0.71[a]	5.3[a]	525	11.8
	C_5H_5N	3.0[b]		780	
		3.33[c]	15.9[c]	865	8.4
		7.20[d]	13.3[d]	1870	11.0
				1170[h]	9.7[h]
	MeCN	1.22[b]		7.50	
		2.6[e]	9.4[g]	1610	9.1
				1180[h]	
Me_3CSH	$(CH_2)_2O$	0.074[f]	3.8[f]	1.98	35.3
	C_5H_5N	0.139[a]	4.0[a]	4.79	33.7
	MeCN	0.189[a]	4.1[a]	9.58	31.4

[a] Ref. 27. [b] Ref. 28. [c] Ref. 29. [d] Ref. 30. [e] Ref. 31. [f] Ref. 9. [g] Ref. 32. [h] Average value.

two-step exchange mechanism involving (i) the dissociation of solvated molecules of MeOH or C_4H_9SH and (ii) the formation of a four-centre complex, is proposed. Hydrogen exchange *via* a four-centre complex is probably the rate-limiting step. The contribution of tunnelling to the two hydrogen motions is small. The rate constant for complex formation increases with increasing polarity of the solvents.

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