

nondiastereoisomeric systems in which the A-B discriminations arise from nearest-neighbor interactions such that a particular B can interact with a number of A and vice versa. The equilibrium conditions are determined by a balance between the racemization entropy favoring the racemate, and the discrimination energy term favoring the more stable enantiomer of A.

The source of the discriminations is postulated to be twofold: chiral perturbation of local solvent lattice structure between A and B; and purely electric dispersion terms varying with separation as R_{AB}^{-9} . It is hoped that future experimental studies will be directed to eliciting which of these two mechanisms leads to the predominant discrimination in aqueous systems.

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Base-Catalyzed Isotopic Exchange of Molecular Hydrogen. 4.¹ Hydrogen Isotope Effects in the Dimethyl Sulfoxide–Water System

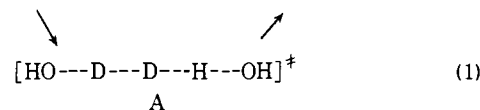
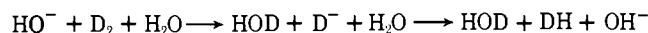
E. Buncel,*² E. A. Symons,*³ and R. A. More O'Ferrall*⁴

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6, Chalk River Nuclear Laboratories, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada KOJ 1J0, and the Department of Chemistry, University College, Belfield, Dublin 4, Ireland.
 Received March 21, 1977

Abstract: Isotope effects for the hydrogen reacting as a hydride ion in the exchange reaction $\text{HO}^- + \text{D}_2 + \text{H}_2\text{O} \rightarrow (\text{HOD} + \text{D}^- + \text{H}_2\text{O}) \rightarrow \text{HOD} + \text{DH} + \text{OH}^-$ in H_2O - Me_2SO mixtures vary smoothly in the range 1.18–1.65 between 0 and 96.9 mol % Me_2SO , passing through a maximum at 65 mol % Me_2SO . Despite the smallness of the effects, model calculations suggest that they are consistent with rate-determining hydrogen transfer. The low zero point energy difference between isotopically substituted hydrogen molecules can give maximum isotope effects lower by a factor of 3 than in reactions of C–H, O–H, or N–H bonds. For reaction via a hydride intermediate the hydrogen separating as a hydride ion is not subject to tunnelling or a Westheimer effect, while $k_{\text{H}}/k_{\text{D}}$ for the transferred hydrogen, which is also small, should be sensitive to the low equilibrium isotope effect for its reaction ($K_{\text{H}}/K_{\text{D}} = 0.26$). In the more probable single step exchange mechanism, concerted hydrogen transfer reduces $k_{\text{H}}/k_{\text{D}}$, and a nonlinear configuration for the transition state may reduce it further. The possibilities of "hydride character" in the concerted transition state, $[\text{HO}---\text{H}---\text{H}---\text{OH}]^\ddagger$, and of formation of $\text{H}-\text{H}-\text{OH}^-$ as an intermediate are considered.

Investigation of isotopic exchange between molecular hydrogen and H_2O in the condensed phase is of interest both from a theoretical viewpoint and also in the potential that the method could offer for separation of the deuterium isotope.⁵ The exchange is extremely slow in pure water, even at elevated temperatures, but it is catalyzed by the hydroxide ion.^{6–8} We have found that the catalyzed reaction is accelerated by using dimethyl sulfoxide (Me_2SO) as a cosolvent,^{9,10} although the increase in rate with increased Me_2SO content is not as large as in the case of many reactions involving rate-determining proton transfer.^{11,12}

The mechanism of hydroxide catalysis, both of the isotope exchange and of the related para- to ortho-hydrogen conversion, has been extensively investigated,^{1,6–10,13–16} but the detailed course of the reaction remains unsettled. Wilmarth⁶ suggested that reaction occurs via a hydride intermediate (eq 1) or by a single concerted step through transition state A. He preferred the stepwise mechanism on the grounds that exchange is not subject to acid catalysis, and that the estimated



energy of formation of $\text{H}^-(\text{aq})$ from H_2 was less than the activation energy of 24 kcal for the reaction.⁶ Olah et al. have more recently reported¹⁷ that exchange does occur slowly in "magic acid" systems.

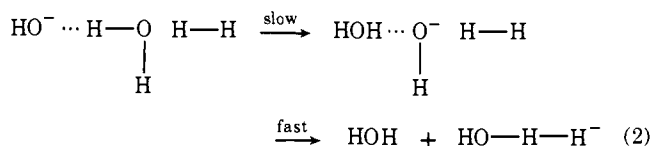
Subsequently, Ritchie reestimated the energy of formation of the hydride ion as 55 kcal, which would favor a concerted mechanism.¹⁴ However, Ritchie also noted^{14,18} that the observed activation energy corresponds to estimates of the energy for removing one water molecule from the solvation shell of the hydroxide ion.¹⁹ Calculations of the potential energy surface for reaction of H_2 with a hydroxide ion in the gas phase show an initial reaction without activation energy and exothermic by 12 kcal/mol to form a stable HHOH^- ion.¹⁴ Ritchie sug-

Table I. Kinetic Data and Isotope Effect Values

Mol % Me ₂ SO	Me ₄ NOH, M	k_{D_2} min ⁻¹ × 10 ³ at 338 K	k_{HD}	$2k_{HD}/$ $k_{D_2}^a$
0.0 ^b	(0.1–0.8 KOH)			1.18 ^b
20.2	0.46	0.121	0.081	1.34
40.1	0.36	0.552	0.390	1.41
59.0	0.42	2.87	2.34	1.63
67.9	0.30	2.52	2.06	1.64
67.9	0.30	3.00	2.43	1.62
77.9	0.27	6.85	5.57	1.63
87.5	0.10	4.20	3.18	1.52
87.5	0.10	4.33	3.39	1.56
87.5	0.10	4.08	3.18	1.56
87.5	0.10	4.07	3.16	1.55
96.9	0.032	5.47	4.12	1.51
96.9	0.022	4.00	3.01	1.51

^a The statistical factor of 2 (ref 22) is used; estimated error in values is ± 0.03 . ^b Derived as explained in text from data of Wilmarth et al. (ref 6).

gested that the same ion is formed in solution and that its unactivated formation allows desolvation and association of hydroxide with H₂ to become rate determining. This is shown in the potential energy profile of Figure 1. The desolvation step can be imagined as occurring either by a direct displacement of H₂O by H₂ in the solvation shell of OH⁻,¹ or as accompanying a Grotthuss type proton transfer (first step of eq 2), in



which relaxation of the solvent is rate determining. In principle, formation of H-H-OH⁻ makes Ritchie's mechanism different from the concerted mechanism, but as the transition state for hydrogen transfer remains the same the chief point of distinction lies in whether or not hydrogen transfer is rate determining.

The relatively weak medium basicity dependence of the exchange rate in H₂O–Me₂SO mixtures,⁹ and also the measured enthalpies of transfer of the exchange transition state from water to aqueous Me₂SO,¹ suggest that formation of the transition state involves minimal desolvation of the hydroxide ion, which would be consistent with Ritchie's mechanism.¹ However, these results may also be reconciled with rate-determining hydrogen transfer if it is assumed that in the transition state negative charge is largely localized on the terminal hydroxyl groups.¹ Apparently more compelling evidence, cited by Ritchie, is the magnitudes of hydrogen isotope effects observed in the reaction.¹⁸ For substitution of either atom of the hydrogen molecule k_H/k_D is less than 1.5. This is much smaller than normally observed in hydrogen transfer reactions but is what might be expected of rate-determining desolvation, in which there is no formation or breaking of covalent bonds to the isotopically substituted molecule.

Because of the mechanistic significance of the isotope effects we have extended their measurement to H₂O–me₂SO mixtures of widely varying medium basicity, and have carried out model calculations to determine more precisely the magnitude to be expected for a primary isotope effect involving molecular hydrogen.

Experimental Section

The procedure employed in the isotope exchange runs involving molecular deuterium and alkaline aqueous Me₂SO solutions has been given previously.^{1,10} Some runs at selected solvent compositions were

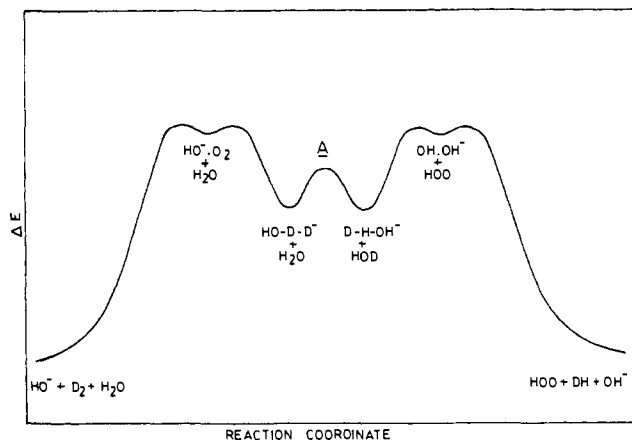


Figure 1. Potential energy profile for base-catalyzed isotopic exchange occurring via the addition complex mechanism (eq 2).

Table II. Comparison of Experimental D₂, HD, and H₂ Data in a Typical Kinetic Run (67.9 mol % Me₂SO, 0.30 M Me₄NOH) with Theoretical Values Obtained by Computer Calculation Using $k_{D_2} = 2.52 \times 10^{-3} \text{ min}^{-1}$. Best Fit $k_{HD} = 2.06 \times 10^{-3} \text{ min}^{-1}$

Time, min	% H ₂		% HD		% D ₂	
	Theor	Exptl	Theor	Exptl	Theor	Exptl
6	0.03	0.00	3.05	2.60	96.92	97.40
72	1.41	1.60	16.52	16.10	82.07	82.30
144	4.68	5.00	26.87	26.30	68.45	68.70
261	12.47	12.90	36.56	36.40	50.97	50.70
300	15.48	15.60	38.32	38.20	46.20	46.30
339	18.61	18.90	39.51	39.50	41.88	41.60
366	20.82	20.70	40.05	40.00	39.12	39.20
390	22.81	22.50	40.36	40.40	36.83	37.20
450	27.82	27.60	40.52	40.60	31.66	31.80
480	30.32	29.90	40.33	40.50	29.35	29.60

followed for up to 3 half-lives, with as many as ten hydrogen samples being taken per run. Analysis by mass spectrometry gave the mole percent D₂, HD, and H₂ in these vapor phase samples: the rate constants obtained directly from log (mole percent D₂) vs. time plots were converted to in-solution values by multiplying by the factor (total moles D₂ in the system)/(moles of D₂ dissolved in the liquid phase) in the normal manner.^{1,10} The base concentration was constant for a given solvent system but was varied from one solvent to another so as to bring the reaction rate within a conveniently measurable range (Table I). In the Me₂SO rich media, base-catalyzed equilibration of the hydrogen isotopes of CH₃SOCH₃ and H₂O molecules occurs readily so that the overall effective H:D ratio remains large under all conditions of exchange.²⁰

The observed trend in the relative analyses for D₂, HD, and H₂ was consistent with a simple consecutive pseudo-first-order kinetic system. Thus, during a run the D₂ level decreased in an exponential manner, the HD increased to a maximum (generally about 40 mol %) before declining, while the H₂ concentration increased steadily. It was thus possible to determine k_{HD} by the following procedure. First, k_{D_2} was obtained from a least-squares treatment of the D₂ vs. time data as before. A computer program based on the equations for a consecutive first-order system²¹ was then utilized to calculate the expected percent HD vs. time data from this k_{D_2} value and an initial estimate of k_{HD} . By means of an iterative process, the experimental and calculated HD data were compared, and the value of k_{HD} was adjusted incrementally to minimize the average deviation between the two sets. The data obtained for a sample run are given in Table II.

Results and Previous Isotope Measurements

The kinetic data obtained are given in Table I. The rate constants measured were for the stepwise exchange of D₂ with H₂O at 65 °C (eq 3).

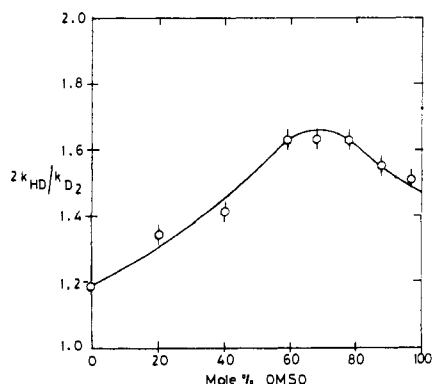
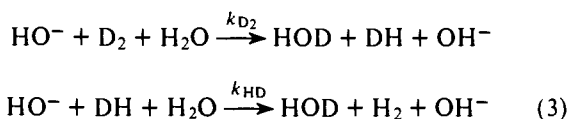
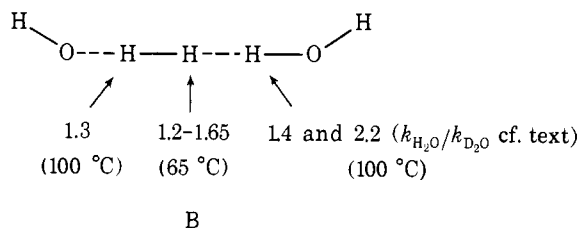


Figure 2. Medium dependence of kinetic isotope effect in Me₂SO-water system.



Combination and correction for the symmetry number²² of 2 for D₂ give a kinetic isotope effect $k_{\text{H}}/k_{\text{D}} = 2k_{\text{HD}}/k_{\text{D}_2}$ which can be seen from the stoichiometry of the exchange reactions to refer to the hydrogen reacting as a hydride ion. The variation of the isotope effect with solvent composition is shown in Figure 2. Errors in the isotope effects were estimated to be ± 0.03 . The value for pure water was derived from the rate constant data of Wilmarth et al.⁶ at 100 °C using the equation $k_{\text{HD}}/k_{\text{D}_2} = \exp(\Delta E_a/RT)$ to convert it to 65 °C.

Combining the present results with the more fragmentary earlier measurements, isotope effects for substitution at different isotopic positions can conveniently be summarized under the transition state formulation B (although B is not intended



to imply a mechanism for the reaction). For the hydrogen transferred from H₂ as a proton $k_{\text{H}}/k_{\text{D}} = 1.3$ was obtained from measurements of the rate constants k_{HD} for exchange of HD and k_{H_2} for conversion of para to ortho hydrogen.⁶ The solvent isotope effect $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ comes from rates of para to ortho conversion in H₂O and D₂O and includes contributions from substitution of all hydrogens other than those of the H₂ molecule. The values of 1.4 and 2.2 for the solvent isotope effect had to be crudely estimated from measurements in different laboratories,^{6,15,16} but the other isotope effects must be considered reliable. It is unlikely that the high temperature is significant in contributing to the small effects because similar values are seen at -50 °C in the analogous exchange reaction between hydrogen molecules and liquid ammonia.²⁵

Discussion

Two points are apparent from the dependence of $k_{\text{H}}/k_{\text{D}}$ upon the Me₂SO content of the medium in water-Me₂SO mixtures shown in Figure 2 and the summary of isotope measurements in B. Firstly, the generality of small isotope effects in the hydroxide-catalyzed exchange of molecular hydrogen is clearly established. For isotopic substitution in the hydrogen molecule, measurements under a wide range of conditions yield isotope effects within the limits 1.2-1.65. Secondly, for the

Table III. Isotopic Partition Function Ratios,^a Excluding Symmetry Numbers, at 25 °C

	ZPE _R ⁻¹	MMI _R ⁻¹	Q _D /Q _H
>C-H->C-D	32.1	1.10	36.0
H ₂ -HD	4.03	2.45	9.86
HD-D ₂	5.23	2.31	12.07
X-H-X-D ^b	9.00	2.00	18.00
H-D	1.00	2.83	2.83
H ₂ O-HDO	32.10	1.02	37.74
HDO-D ₂ O	33.20	1.02	38.87

^a See "Details of Calculations" for explanation. ^b With harmonic force constant for H₂ but X has infinite mass. Lack of anharmonic corrections to HX should affect difference from H₂-HD and HD-D₂ by only 2-3%.

measurements in aqueous Me₂SO a distinct maximum in $k_{\text{H}}/k_{\text{D}}$ is observed at a composition of approximately 65% Me₂SO.

Such behavior is quite unusual for primary isotope effects. Small effects are possible and have been associated with reactant-like or product-like transition states,²³ but in going from water to Me₂SO one would expect the huge change in basicity of the hydroxide ion, revealed by *H*⁻ measurements,¹² to modify the transition state and lead to a much larger increase in isotope effect than observed.²⁴ Moreover, while an isotope maximum is normally characteristic of primary isotope effects, in this case the magnitude at the maximum is so small as to be quite uncharacteristic.

On the face of it the results favor Ritchie's mechanism, with formation of what Kreevoy²⁶ calls the "reaction complex" rather than hydrogen transfer being rate determining. Before drawing a firm conclusion, however, it is necessary to make a proper estimate of the isotope effects to be expected of rate-determining proton transfer in this system.

Isotope Contributions from Reactants. An obvious difference of primary isotope effects for exchange of molecular hydrogen from those normally measured in organic reactions is that the reacting hydrogen originates not from a C-H, O-H, or N-H bond but from a hydrogen molecule. Isotope effects may be expressed in terms of partition functions for isotopic reactants and transition states, Q and Q^\ddagger , and a tunnelling correction:

$$\frac{k_{\text{H}}}{k_{\text{D}}} = \frac{Q_{\text{H}}^\ddagger Q_{\text{D}}}{Q_{\text{D}}^\ddagger Q_{\text{H}}} \text{TUN} \quad (4)$$

From Table III, which lists values of partition function ratios, $Q_{\text{D}}/Q_{\text{H}}$, for deuterium and hydrogen modifications of various stable molecules, it can be seen that for H₂ and HD $Q_{\text{D}}/Q_{\text{H}}$ is little more than one-quarter that of a typical C-H bond.

The origin of this difference is shown by separating the contribution of zero point energy to $Q_{\text{H}}/Q_{\text{D}}$ from that of rotational and translational partition functions. The zero point energy (ZPE_R²⁷) depends upon the H and D vibration frequencies,

$$\text{ZPE}_R = \exp\left\{\frac{\sum h(\nu_{\text{H}} - \nu_{\text{D}})}{2kT}\right\} \quad (5)$$

which are determined by force constants and atomic masses, as shown for a diatomic molecule:

$$\nu_{\text{H}} = \frac{1}{2\pi} \sqrt{f \left(\frac{1}{m_{\text{H}}} + \frac{1}{m_{\text{X}}} \right)} \quad (6)$$

For hydrogen isotope effects the zero point energy is often the only important contribution to $Q_{\text{H}}/Q_{\text{D}}$, but with simple hydrides, including hydrogen molecules, translational and rotational contributions must also be considered.²³ These can be expressed either as ratios of molecular masses and moments of inertia (MMI_R²⁷) or, by use of the product rule,²⁸ as ratios of vibration frequencies:

$$\text{MMI}_R = \left(\frac{m_H}{m_D}\right)^{3/2} \prod_{3n-6} \frac{\nu_H}{\nu_D} \quad (7)$$

Thermal excitation of hydrogen vibrations (EXC_R) is important only for vibrations of unusually low frequency.

From Table III we can see that the contribution of zero point energy (ZPE_R^{-1}) to k_H/k_D for H_2 and HD is only one-eighth that of a typical C-H bond. In part this is because H_2 possesses no bending vibrations and in part because isotopic substitution occurs next to another hydrogen rather than next to a heavy atom. The latter factor leads to an isotopic shift in frequency of $\sqrt{3}/2$ (0.866) instead of $1/\sqrt{2}$ (0.707), as is apparent from eq 6 and is illustrated in Table III by comparison of ZPE_R^{-1} for H_2 and HD with that for the hypothetical molecules HX and DX in which the force constant is the same but the mass of X is infinite. The slightly larger difference in zero point energy between HD and D_2 than between H_2 and HD is also due to the greater mass of D than H. The small zero point energy contribution to Q_D/Q_H for hydrogen molecules is in some degree compensated by isotopically sensitive rotational and translational partition functions (eq 8) but far from completely so.

$$\text{MMI}_R = (M_{\text{H}_2}/M_{\text{D}_2})^{3/2} (I_{\text{H}_2}/I_{\text{D}_2}) \quad (8)$$

If there were no compensation in the transition state, the low values of $Q_{\text{DH}}/Q_{\text{H}_2}$ and $Q_{\text{D}_2}/Q_{\text{DH}}$ would alone account for unusually small isotope effects. Thus the possibility that the observed effects are consistent with primary isotope effects has to be taken seriously and in what follows we attempt the more difficult part of an evaluation of kinetic isotope effects, estimating partition function ratios and tunnelling corrections for transition states.

Isotope Contributions from Transition States. Calculation of isotopic partition function ratios for transition states requires assignments of force constants and geometries to suitable transition state models. Such assignments must in some degree be arbitrary but are here based on a procedure^{29,30} that gives reasonable isotope effects for "nonconcerted" hydrogen transfer between heavy atoms, and in a general way takes into account the results of calculations from ab initio and semi-empirical potential surfaces for simple hydrogen transfer reactions.^{31,32}

For hydrogen transfer from carbon, oxygen, or nitrogen the calculated isotope effects are dominated by the Westheimer effect.³² That is, they show a maximum value roughly corresponding to the zero point energy difference between H and D stretching vibrations in the reactants for a transition state in which the partial bonds to the reacting hydrogen are of equal strength.^{32,33} For this transition state, which is referred to as symmetrical, the only stretching vibration in which the hydrogen is in motion is that for the reaction coordinate (ν_L^\ddagger). Hence isotopic substitution leads to no change of zero point energy in the stretching vibrations, and it follows that contributions to the isotope effect from zero point energy changes in bending vibrations, in the transition state and in the reactants, and from tunnelling substantially cancel. In practice force constants are assigned to yield quite small tunnelling corrections and this leads to transition state bending frequencies not much greater than in the reactants and comparable with those of hydrogen bonds.

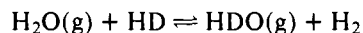


With smaller or larger degrees of hydrogen transfer the force constants relax from their values in the symmetrical transition state and approach values in the reactants or products. This leads to a smooth variation of the isotope effect with the degree

of hydrogen transfer from $1.0 - (k_H/k_D)_{\text{sym}} - K_H/K_D$, where $(k_H/k_D)_{\text{sym}}$ and K_H/K_D are respectively the isotope effect for a symmetrical transition state and the isotope effect upon the equilibrium constant for the reaction. The main factor responsible for the variation is a shift in isotopic sensitivity from the reaction coordinate mode to a real stretching mode (ν_R^\ddagger). The product rule constrains the combined isotopic sensitivity of the two frequencies to $\sim 1/\sqrt{2}$. In previous papers^{29,30,34} k_H/k_D has been calculated for various degrees of hydrogen transfer, but given the limitations of the model, $(k_H/k_D)_{\text{sym}}$ and K_H/K_D should normally suffice, and this simplification is followed here.³⁵

The Westheimer effect applies only to linear transition states, and for nonlinear structures with comparable force constants much smaller isotope effects are calculated.³⁴ Small isotope effects and nonlinear transition states may be a feature of hydride transfer reactions³⁶ and this could be a factor in the H_2 -hydroxide isotope exchange. The most controversial aspect of the transition state model is probably the magnitude of the tunnelling correction. Detailed discussions of this point are available.^{23,37,38}

Details of Calculations. Partition function ratios for the stable molecules in Table III were calculated from vibration frequencies, making use of the product rule. For H_2 and H_2O (gas) full anharmonic corrections to the zero point energy were included, in the manner described by Wolfsberg.^{39,40} For H_2O , HDO, and D_2O harmonic frequencies were based on Kuchitsu and Bartell's valence force field,⁴¹ and the anharmonic corrections were those listed by Wolfsberg, Massa, and Pyper.⁴⁰ The value of 3.54 at 25 °C ($\text{MMI}_R = 0.736$, $\text{EXC}_R = 1.00$) calculated for the exchange equilibrium



compares very well with the value of 3.53 based on a least-squares analysis of experimental measurements at various temperatures, although the precise agreement probably reflects cancellation of neglected corrections to the classical treatment of rotations for H_2 and use of the Born-Oppenheimer approximation.⁴² Partition function ratios for liquid water were obtained using $p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}} = 1.156$ and $p_{\text{H}_2\text{O}}/p_{\text{HDO}} = 1.079$ at 25 °C.⁴³ Separation into ZPE, MMI, and EXC was made on the assumption that the contributions were in the proportions calculated for a tetrahedrally hydrogen bonded water model.⁴⁴ Q_D/Q_H for the C-H reactant was based on a fractionation factor of 0.94 with respect to liquid water (cf. Table V, p 216 of ref 23); the corresponding values of MMI_R , ZPE_R , and EXC_R are reasonable but arbitrary. Symmetry numbers are excluded from the partition function ratios, as they are from calculated isotope effects.

For transition states $Q_D^\ddagger/Q_H^\ddagger$ was based on harmonic frequencies calculated from assigned geometries and force constants. Usually the transition state involved symmetrical binding of the reacting hydrogen and for nonreacting bonds bond lengths and force constants were the mean of their values in reactants and products. For reacting bonds bond lengths were obtained from Pauling's relationship;²⁹ stretching force constants ($f_1 = f_2$) were 1.0 or 2.0 mdyne/Å; force constants for bending about a reacting hydrogen were the same as in the bifluoride ion²⁹ (0.212 mdyne/Å); and force constants for bending about atoms flanking the reacting hydrogen were one-quarter their values in reactants or products.⁴⁵ The interaction force constant between reacting bonds, f_{12} , was most commonly chosen to give a tunnelling correction of $\sim 40\%$ (and $k_H/k_D = 7-8$) for hydrogen transfer between heavy atoms. The tunnel correction used was a truncated version of Bell's expression³⁷ for a parabolic barrier:

$$\Gamma = 1 + \frac{u^2}{24} + \frac{7u^4}{5760} \quad \text{where } u = h\nu_L^\ddagger/kT$$

Table IV. Calculated Isotope Effects for Hydrogen Transfer to a Hydroxide Ion at 25 °C

Reactants ^a	Symmetrical transition State Equilibrium				
	MMI	TUN	$(\frac{k_H}{k_D})_{\text{sym}}^b$	MMI	K_H/K_D
C-C-D + OH ⁻	1.05	1.39	7.43	1.08	0.95
D-H + OH ⁻	1.39	1.02	1.53 ^c	0.87	3.49
H-D + OH ⁻	1.94	1.41	2.44	2.40	0.261
D-D ^d + OH ⁻	2.75	1.42	4.39	1.96	1.12
X-D ^e + OH ⁻	1.97	1.39	4.19	1.96	0.477

^a For transfer of a proton to hydroxide. The transferred atom is that adjacent to OH, e.g., C-C-D + OH⁻ → C-C⁻ + DOH. The isotopically substituted atom is indicated by D. Isotopic transition states are shown in Table V. ^b k_D refers to the reactants as written, k_H to the reaction with D replaced by H. ^c Increasing $f_{DH} = f_{HO}$ from 1.0 to 2.0 mdyne/Å in the transition state reduced k_H/k_D to 1.06. ^d k_{D_2}/k_{H_2} . ^e The mass of X is 1000 for the kinetic isotope effect and infinite for the equilibrium.

The correction depends on the reaction coordinate frequency ν_L^\ddagger which in the symmetrical case is determined by $f_1 - f_{12}$ (since $\nu_L^\ddagger \approx \{(f_1 - f_{12})/m_H\}^{1/2}/2\pi$). It corresponds roughly to the correction for a one-dimensional Eckart barrier for which $2\pi V^\ddagger/h\nu_L^\ddagger = 6$ where V^\ddagger is the barrier height.⁴⁶ Its use in qualitative estimates of isotope effects is probably justified when no large variations in the extent of tunnelling occur.

The only difference in force constants affecting motion of isotopically substituted atoms between symmetrical transition states for C-H and hydrogen-molecule reactants was for bending at atoms flanking the reacting hydrogens, and these force constants make only a small contribution to the isotope effect. Where transition states other than symmetrical were considered, force constants and bond lengths were allowed to vary with the order z between the reacting hydrogen and attacking base, as described previously;²⁹ for nonreacting bonds values were weighted means of those in reactants and products, and for reacting bonds decreased from their reactant or product values with the square of the bond order; further details are given in footnotes to the tables.

For stretching force constants the second-power dependence upon bond order contrasts with dependence on the first power used previously.²⁹ The change is consistent with the low transition-state force constants calculated for hydrogen atom transfer reactions (e.g., Table VIII on p 245 of ref 23) and the low stretching force constant for HF₂⁻ relative to HF (2.3 compared with 9.7), but it has only a very minor effect upon calculated values of k_H/k_D for a reacting hydrogen.

Although experimental measurements were made at 65 °C, the calculated isotope effects are normally reported for 25 °C, the temperature at which isotope effects are most commonly quoted. The temperature dependence of the effects is considered separately.

Calculated Isotope Effects and Reaction Mechanism. The aim of the calculations was to compare isotope effects upon hydrogen transfer from a hydrogen molecule with those upon transfer from a heavy atom, typically carbon, in a polyatomic molecule, with special reference to mechanisms of hydroxide catalyzed isotope exchange of hydrogen molecules with water. Comparisons are made between calculations for "symmetrical" hydrogen and heavy-atom transition states and between the corresponding reaction equilibria, using identical or comparable force constants for the transition states where motion of an isotopically substituted hydrogen is involved. Calculated isotope effects are presented first for the stepwise mechanism of hydrogen exchange. Although this mechanism is perhaps not the most likely one, it simply illustrates the procedure and

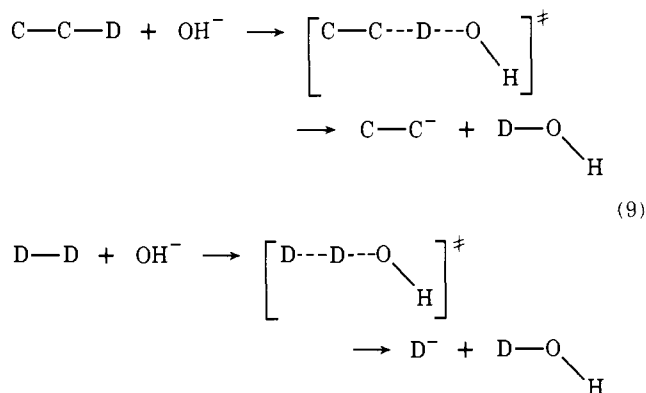
Table V. Isotopically Sensitive Vibration Frequencies (cm⁻¹) for Symmetrical Transition States^a

Transition state	Stretches	Bends	
		In plane	Out of plane
C-C--H--OH	834i 444	1448	1344
C-C--D--OH	598i 444	1065	977
H-H-OH	867i 1367	1467 606	1387
D-H-OH	857i 1006	1400 577	1303
H-D-OH	632i 1362	1143 605	1092
D-D-OH	624i 1000	1060 575	986

^a Stretching force constants of reacting bonds 1.0 mdyne/Å; stretch-stretch interaction force constant 1.2 mdyne/Å; bending force constants $f_{CCH} = 0.24$, $f_{CHO} = 0.313$, $f_{HHO} = 0.225$, $f_{HOH} = 0.175$ ergs/rad² × 10⁻¹¹. Vibrations were assigned from inspection of eigenvectors

leads on to consideration of the more probable but more complicated concerted mechanism.

A. Exchange via a Hydride Intermediate. The reaction of hydrogen with hydroxide to yield a hydride intermediate, i.e., the rate-determining step of the stepwise isotope exchange mechanism, is shown in eq 9 together with the heavy atom reaction with which it is compared. Positions of deuterium substitution for which isotope effects were calculated are denoted D.



Values of MMI_R , ZPE_R , and Q_D/Q_H needed for calculating equilibrium isotope effects are listed in Table III. Q_D/Q_H for the hydride ion was calculated assuming free translations, and insofar as H⁻ is probably strongly solvated may be a crude overestimate. Isotope effects $(k_H/k_D)_{\text{sym}}$, together with tunnelling factors and net MMI contributions obtained by combining Q_D/Q_H for the reactants and $Q_D^\ddagger/Q_H^\ddagger$ for a "symmetrical" transition state, in which the force constants of the partial bonds to the reacting hydrogen are equal, are shown in Table IV. The first row of the table refers to hydrogen transfer from carbon, and the next three refer to reactions of hydrogen molecules substituted at either or both isotopic positions; the last row shows results for a hypothetical reactant X-H with the same force constant as H₂ but an atomic mass of 1000 for X. Also shown are calculated equilibrium isotope effects, and we assume that $1.0 - (k_H/k_D)_{\text{sym}} - K_H/K_D$ expresses the range of isotope effects available to each reaction for different degrees of hydrogen transfer in the transition state.

Force constants and isotopically sensitive vibration frequencies are collected in Table V and its footnotes. For the reacting bonds in the symmetrical transition state the force constants are $f_1 = f_2 = 1.0$ mdyne/Å. For the hydrogen transferred between H₂ and OH⁻ as a proton the magnitudes of f_1 and f_2 only indirectly affect k_H/k_D through dependence of the tunnel correction upon $f_1 - f_{12}$, but for the hydrogen separating as a hydride ion an increase in these force constants decreases the isotope effect.

carbons, with $f_1 = 1.0$ and $f_2 = 2.0$ mdyn/Å. The positions of isotopic substitution are indicated by D in the appended transition state structures, and the second and third sets of figures refer respectively to k_{H_2}/k_{HD} and k_{HD}/k_{D_2} . For $y = 1.2$ the transition states are directly comparable with those for hydrogen transfer from carbon and H_2 to hydroxide in the first and third rows of Table IV (although the reacting hydrogen is now a hydride ion rather than a proton). Additional weak bending force constants in C decrease the isotope effects slightly, and with three adjacent hydrogens there is a compensating increase in frequency and decrease in isotopic sensitivity for the bending vibrations. However, the isotope effects for the "carbon" and "hydrogen" transition states still differ by a factor of 3, reflecting the difference in Q_D/Q_H for H_2 and C-H reactants.⁵¹ As expected, increasing y increases isotope effects by increasing tunnelling but leaves the difference unaffected.

Increasing x from zero introduces the additional interaction force constants f_{12} into the transition state. An increase in f_{12} relative to f_{23} decreases motion of the central hydrogen in the reaction coordinate and causes it to move in a real stretching mode. This leads to isotopically sensitive zero point energy in the stretching vibrations and, under constraint of the product rule, diminished isotopic sensitivity for the reaction coordinate. As shown in Table VIII for $y = 1.2$, k_H/k_D decreases, despite the increase in the calculated tunnelling corrections (TUN) due to an increase in magnitude of the reaction coordinate frequency.⁵² The effect is greater for the transition state in which the flanking atoms are hydrogens, and the decrease in k_H/k_D from 2.2 to 1.0 as x increases from 0 to 1.4 in this case compares with a decrease of 7.0 to 5.4 for the carbon transition state.

For the flanking hydrogens the effect of increasing x upon isotopic substitution complements that for the central atom. Motion in the reaction coordinate increases and, as shown in Table VIII, k_H/k_D increases. When $x = 0$ there is no hydrogenic motion in the reaction coordinate and the low value of Q_D/Q_H for the reactants gives a substantial inverse isotope effect, $k_H/k_D = 0.36$, irrespective of y . Thus the effect of a large value of x is to convert an inverse isotope effect into a normal one, although even for large values of x k_H/k_D remains close to 1.0.

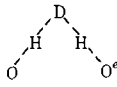
Thus as anticipated by Bell⁵³ and confirmed by Katz and Saunders' calculations,⁵⁰ concerting motion of a reacting hydrogen with that of other atoms is a potent factor moderating isotope effects. For a nonreacting hydrogen the isotope effect is correspondingly enhanced. Interestingly, in the hydroxide catalyzed isotope exchange the small isotope effect measured for the central hydrogen (1.2–1.65) and "large" effect for a flanking hydrogen (1.3) are both consistent with strongly concerted hydrogen transfers.

There is therefore qualitative agreement between experiment and calculations, and it is worth considering to what extent the calculated results depend upon the specific force constants and symmetrical structure assigned to the transition state, and also whether they can account for the distinctive maximum in k_H/k_D observed with changing hydroxide basicity (Figure 2).

As discussed in more detail below the greater sensitivity of the reaction to base than acid catalysis^{6,16} may indicate that the OH^- groups in the transition state are strongly bound to their adjacent hydrogens. The values of 1.0 and 2.0 mdyn/Å used for f_1 and f_2 , respectively, are consistent with this, but k_H/k_D is little affected by increasing f_2 to 5.0 mdyn/Å or indeed by using equal values of f_1 and f_2 .

The effect of asymmetry in the transition state may be seen by calculating equilibrium isotope effects, K_H/K_D , and considering that $1.0 - (k_H/k_D)_{sym} - K_H/K_D$ represents the limits to variation of k_H/k_D with degree of hydrogen transfer in the

Table VIII. Isotope Effects and Tunnel Corrections at 25 °C for Concerted and Nonlinear Transition States^a

Transition state	x	TUN	$(k_H/k_D)_{sym}$
C--C--D--C--C	0	1.40	6.98
	1.0	1.59	5.78
	1.4	1.64	5.37
O--H--D--H--O ^{b,c}	0	1.42	2.16
	1.0	1.60	1.21
	1.4	1.61	0.96
O--D--H--H--O ^{b,d}	0	1.01	0.36
	1.0	1.34	0.96
	1.4	1.37	1.35
	0	1.20	1.21
	1.0	1.45	0.71
	1.4	1.37	0.57

^a $f_{12} = x\sqrt{f_1 f_2}$ in C; $y = 1.2$; other force constants as in Table VII.
^b Reaction coordinate frequencies ($\nu_L^\ddagger(H)$ cm⁻¹) and isotopic sensitivities (in brackets) for $x = 0, 1.0$, and 1.4, respectively: 865 (b 1.39, c 1.01), 2206 (c 1.15, d 1.09), 2760 (c 1.12, d 1.10). $e_y = 1.2$, H-D-H angle is 90°. Force constants unchanged from linear transition state.

transition state. Only if K_H/K_D is large are large values of k_H/k_D likely, for product-like transition states. Neglecting symmetry numbers as usual, for the central hydrogen, for which k_{HD}/k_{D_2} is the kinetic isotope effect determined experimentally, we have from eq 3

$$\frac{K_{HD}}{K_{D_2}} = \frac{Q_{H_2} Q_{D_2}}{Q_{HD}^2} = 1.21 \quad (10)$$

and it is clear that the value is too close to 1.0 to cause significant variation from the small effect calculated for symmetrical transition states. However, for the flanking hydrogens, for which k_{H_2}/k_{HD} is measured,

$$\frac{K_{H_2}}{K_{HD}} = \frac{Q_{HD} Q_{H_2 O}}{Q_{H_2} Q_{HDO}} = 0.26 \quad (11)$$

and K_H/K_D is substantially inverse. The calculation is for 25 °C and at the temperature of measurement, 100 °C, the value is closer to unity (0.4 rather than 0.26) but it is still small enough that for a sufficiently product-like transition state the kinetic isotope effect might be expected to be inverse.

The significant feature of the isotope maximum in Figure 2 is that the observed variation in k_H/k_D (1.2–1.65) is small. It is possible therefore that it results from quite a small variation in force constants, and if so its origin could not easily be determined from model calculations since these distinguish only gross features of isotope effects. Interestingly, however, the calculations indicate that quite large changes in force constants and transition state structure, of the magnitude that might well be expected of the large variations in basicity of the hydroxide ion with changing Me_2SO content of the medium, lead to changes in isotope effect quite small enough to be consistent with those observed. While the calculations do not require an isotope maximum they are fully compatible with it, and the situation contrasts nicely with the Westheimer effect³² for simple hydrogen transfers where experiment and calculations involving comparable changes in force constant show an isotope maximum with large changes in k_H/k_D .

Transfer of hydrogen as a hydride ion could lead to a transition state with a nonlinear arrangement of the reacting bonds. This is usually regarded as a further factor reducing isotope effects^{34,36} and additional calculations in which structure C was modified to give an angle of 90° at the central hydrogen confirmed that this was so irrespective of the magnitude of bending forces constants and despite an increase in f_{23} to maintain the same contribution from tunnelling as in the linear transition state (Table VIII).

drude hydrogen as in D but upon the hydroxyl groups.¹ In extension one may argue that the greater accessibility to solvating molecules of two hydroxyl groups in the transition state compared with one in the reactants perhaps compensates for the delocalization of charge.¹ However, an alternative explanation of the lack of acid catalysis is that the ion H-H-OH⁻ proposed by Ritchie¹⁴ is formed as an intermediate; that is, that the reaction is as shown in Figure 1 but with transition state A the highest point on the potential energy profile. Although not required by the concerted mechanism, the presence of the H-H-OH⁻ ion would remove the necessity of postulating pronounced hydride character in the transition state. It would also account for the dominance of specific hydroxide over general base catalysis,¹ a further experimental point established by Wilmarth,¹³ and would remove the necessity of supposing that the concerted transition state is formed in a termolecular collision. This is an unsatisfactory feature of the simpler mechanism notwithstanding the fact that one of the molecules is a solvent molecule.

It seems that the available results are consistent with a concerted mechanism but that details of the transition state and reaction intermediates remain uncertain. If such a conclusion seems vague in relation to the extensive studies carried out, this is due at least in part to the lack of analogy with more familiar organic or inorganic reactions and to the quite limited structural variations permitted by the reactants.

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