A final point of uncertainty concerns the relative magnitude of the two stretching frequencies ν_1 and ν_3. A number of measurements of crystals of hydronium ion salts have led to the assignment of widely separated frequencies to these two modes.[20] These assignments have not been followed in all such measurements,[22,24] but $H_9O_4^+Br^-$ offers an example of where they have.[23] Giguère's recent demonstration that ν_1 and ν_3 are very closely spaced for solutions of hydronium halides in liquid sulfur dioxide,[28] however, strongly suggests that the same may be true of aqueous solutions. Indeed, this is certainly the normal situation[47] for pyramidal hydrides of the type XH_3. Calculations were carried out, therefore, with the covalent O–H stretching interaction force constant for H_3O^+ taken as zero. Other force constants were unchanged from model **6** (Table VII), and there was no effect on the calculated value of L. For $L = 9.0$, values of $\nu_1(a) = 2530$ and $\nu_3(e) = 2620$ were obtained.

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Solvent Isotope Effects upon Proton Transfer from the Hydronium Ion

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Abstract: Model calculations of solvent isotope effects for reactions of H_3O^+ in H_2O are described. Models for H_2O and H_3O^+ take account of librational modes, and force constants are chosen to yield the constant $L = 9.0$ for the equilibrium $2D_3O^+ + 3H_2O \rightleftarrows 2H_3O^+ + 3D_2O$. Primary and secondary isotope effects $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$ for proton transfer from H_3O^+ are calculated. It is found that as the structure of the transition state is varied from reactant-like to product-like the secondary isotope effect increases monotonically, while the primary isotope effect passes through a maximum. The parameter α defined by $(k_H/k_D)_{II} = L^{-\alpha/3}$ provides a measure of the extent of proton transfer in the transition state. Contributions from "transfer" isotope effects are taken into account. Deviations from the rule of the geometric mean (RGM) for isotopic exchange equilibria are considered in detail within the framework of Bernstein's rules, and are ascribed mainly to contributions from bending vibrations. The deviations are underestimated by harmonic calculations, but calculations and experiment combined yield practical estimates for both D and T fractionation in H_2O and H_3O^+. Deviations are canceled between H_2O and H_3O^+ but cause discrepancies of up to 10% in the fractionation of single exchangeable hydrogens. Their effect upon the separation of primary and secondary kinetic isotope effects for proton transfer from H_3O^+ is tested. Maximum discrepancies between experimental methods based on (i) kinetic dependence in H_2O–D_2O mixtures, (ii) isotope distribution in the products, and (iii) tritium transfer in H_2O and D_2O are again 10% and are associated principally with fractionation of the reacting hydrogen. Neglect of deviations from the RGM does not obscure the strong correlations between isotope effects and transition state structure.

It has been recognized for some time that solvent isotope effects[4,5] upon rate-determining proton transfer from the hydronium ion in H_2O and D_2O comprise two contributions; a primary effect $(k_H/k_D)_I$ from the reacting hydrogen of the H_3O^+ unit, and a secondary effect $(k_H/k_D)_{II}$ from the nonreacting hydrogens.[6,7]

$$H_3O^+ + S \longrightarrow [\underset{II}{H}_2O\text{---}\underset{I}{H}\text{---}S]^{\ddagger} \longrightarrow H_2O + SH^+$$

Methods have been developed for separating the two effects,[8-11] and it has been suggested that $(k_H/k_D)_{II}$ may be related to the equilibrium isotope effect for the reaction[8,12,13] through a free-energy relation of the form $(k_H/k_D)_{II} = L^{-\alpha/3}$, where L is the equilibrium constant for isotope exchange between H_3O^+ and H_2O

$$2D_3O^+ + 3H_2O \rightleftarrows 2H_3O^+ + 3D_2O$$

and α is a parameter analogous to the exponent of the Brønsted relation.[5,13-15]

This is of interest because α may be interpreted as an index of the "extent of proton transfer" in the transi-

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(3) Illinois Institute of Technology.

(4) P. M. Laughton and R. E. Robertson in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, p 399.

(5) V. Gold, *Advan. Phys. Org. Chem.*, 7, 259 (1969).

(6) C. A. Bunton and V. J. Shiner, *J. Amer. Chem. Soc.*, **83**, 3214 (1961).

(7) C. G. Swain and E. R. Thornton, *ibid.*, **83**, 3884 (1961).

(8) A. J. Kresge, *J. Pure Appl. Chem.*, **8**, 243 (1964).

(9) M. Kreevoy and R. A. Kretchmer, *J. Amer. Chem. Soc.*, **86**, 2435 (1964).

(10) A. J. Kresge and D. P. Onwood, *ibid.*, **86**, 5014 (1964).

(11) V. Gold and M. A. Kessick, *J. Pure Appl. Chem.*, **8**, 421 (1964); *Discuss. Faraday Soc.*, **39**, 84 (1965); *J. Chem. Soc.*, 6718 (1965).

(12) M. Kreevoy, P. Steinwand, and W. Kayser, *J. Amer. Chem. Soc.*, **86**, 5013 (1964).

(13) V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960).

(14) M. Kreevoy, *Advan. Phys. Org. Chem.*, **6**, 63 (1968).

(15) W. J. Albery, *Progr. React. Kinet.* **4**, 353 (1967).

Table I. The Relation of Transition State Parameters to Their Limiting Values in Reactants and Products[a]

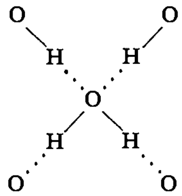
Bond lengths and angles	Stretching force[b] constants	Bending force[b] constants
$r_5 = R_5 - 0.6 \log (1 - z)$	$f_{r_5} = (1 - z)F_{R_5}$	$f_{\varphi_2} = (1 - z)^2 F_{\Phi_2}$
$r_6 = R_6 - 0.6 \log z$	$f_{r_6} = zF_{R_6}'$	$f_{\varphi_3} = (1 - z)^2 F_{\Phi_3}$
$\varphi_9 = 180°$	$f_{r_5 r_6}{}^{c} = (1 + y^2(1 - y)^2)(f_{r_5} f_{r_6})^{1/2}$	$f_{\varphi_{11}} = z^2 F_{\Phi_{11}}'$
$\varphi_{11} = 180°$		$f_{\varphi_{12}} = z^2 F_{\Phi_{12}}'$
$\varphi_{12} = 180°$		$f_{\varphi_9}{}^{c} = f_{\varphi_{10}} = 16y^2(1 - y)^2 F_\beta$

[a] All parameters not listed here have the dependence on z given in the text. [b] Subscripts denote coordinates in **3** to which force constants refer. [c] $y = f_{r_6}/(f_{r_5} + f_{r_6})$.

tion state. In this paper, we report model calculations designed to test the validity of the relation and of some of the assumptions on which it rests.

The Models and Calculations

The method of the calculations is similar to that applied previously to primary isotope effects.[16,17] Vibration frequencies and isotope effects are evaluated from force constants and geometries assigned to models for the reactants, products, and transition state. A suitable model is considered to consist of the minimum number of atoms permitting an adequate representation of the vibrational modes contributing to the isotope effect. The principal new feature of calculations for proton transfer from the hydronium ion in aqueous solution is that librational modes arising from hindered rotations of H_2O and H_3O^+ within the hydrogen-bonded water lattice have to be considered. These modes are known[18,19] to contribute substantially to solvent isotope effects in H_2O and D_2O.



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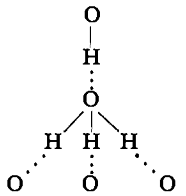

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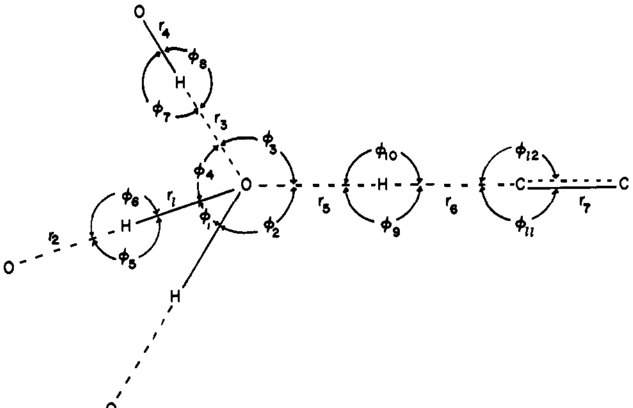
The models **1** and **2** chosen for H_2O and H_3O^+ are described in detail in the preceding paper.[20] Force constants for H_3O^+ were assigned to yield calculated frequencies which, when combined with the frequencies for H_2O, gave the experimentally determined value[19,21] of 9.0 for the equilibrium constant L. The values chosen differed only slightly from those used previously,[20] and it was assumed that isotopic fractionation in the solvation shell of the H_3O^+ unit makes no contribution to the isotope effect. For the substrate, a two-atom "olefinic" fragment C═C was used, which gives a linear carbonium ion species H—C—C$^+$ as product. Adoption of a linear configuration for the product allows a satisfactory treatment of hydrogen bending vibrations while minimizing the complexity of the model. The effectiveness of this approximation in treating bending modes in the product and transition state is discussed in ref 16.

In the transition state, it was supposed that one of the H_3O^+ hydrogens becomes partially bonded to the substrate and that in other respects the geometry is intermediate between that of reactants and products. The structure of the transition state was specified by a parameter z denoting the order of the partial bond between the reacting hydrogen and the substrate. Taking the order of the partial O–H$^+$ bond as $(1 - z)$, and assuming that the bond lengths, angles, and force constants of the transition state depend upon simple functions of z in such a way as to reduce to their corresponding values in reactants and products in the limits that $z \rightarrow 0$ or 1, it was possible to specify the geometry and force field of the transition state almost entirely in terms of z and of the bond lengths, angles, and force constants of the reactants and products. The limiting values of stretching and bending force constants for bonds between C═C and H_3O^+ as $z \rightarrow 0$, and between $^+$C—C—H and H_2O as $z \rightarrow 1$, were taken to be zero.

The bond lengths and angles to be assigned in the transition state are shown in **3**. The model has C_s symmetry and, for clarity, parameters are not duplicated. In most cases, transition state parameters were expressed as the weighted arithmetic mean of their values in reactants and products, *i.e.*



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$$r = zR' + (1 - z)R \qquad \varphi = z\Phi' + (1 - z)\Phi$$
$$f = zF' + (1 - z)F$$

where r, φ, and f denote bond lengths, bond angles, and force constants, and small letters, capitals, and primed capitals refer to the transition state, reactants, and products, respectively. Exceptions, which pertain mainly to the bond lengths and force constants associated with the reacting bonds, are listed in Table I using the above notation and that of **3**. The treatment of these parameters has been described in detail previously,[16] and only minor modifications were made here. However, it may be noted that the maximum value of

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(16) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967).

(17) A. M. Katz and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, 91, 4469 (1969); J. Bigeleisen, *J. Pure Appl. Chem.*, 8, 217 (1964); R. A. More O'Ferrall, *J. Chem. Soc. B*, 785 (1970).

(18) C. G. Swain and R. F. W. Bader, *Tetrahedron*, 10, 182 (1960).

(19) K. Heinzinger and R. E. Weston, *J. Phys. Chem.*, 68, 744 (1964); K. Heinzinger, *Z. Naturforsch. A*, 20, 269 (1965).

(20) R. A. More O'Ferrall, G. W. Koeppl, and A. J. Kresge, *J. Amer. Chem. Soc.*, 93, 1 (1971).

(21) P. Salomaa and V. Aalto, *Acta Chem. Scand.*, 20, 2035 (1966).

Table II. Force Constants for Reactants, Products, and Transition State ($z = 0.5$)

Stretching force constants, mdyn/Å				Bending force constants, (mdyn Å)/rad^2			
Coord	Reactant	Product	TS	Coord	Reactant	Product	TS
r_1	3.65	6.55	5.10	φ_1	0.60	0.65	0.625
r_2	0.3	0.12	0.21	φ_2	0.60	0^a	0.15
r_3	0.02	0.12	0.07	φ_3	0.02	0^a	0.005
r_4	7.0	7.0	7.0	φ_4	0.02	0.067	0.0435
r_5	3.65	0.0	1.825	$\varphi_5 = \varphi_6$	0.08	0.067	0.0735
r_6	0^a	4.8	2.4	$\varphi_7 = \varphi_8$	0.02	0.067	0.0435
r_7	9.7	4.5	7.1	$\varphi_9 = \varphi_{10}$	0^a	0^a	0.19^b
				$\varphi_{11} = \varphi_{12}$	0	0.98	0.245
$r_1r_1{}^c$	0.4	−0.25	0.075				
$r_1r_5{}^c$	0.4	0.0	0.2	$\varphi_1\varphi_2{}^c$	0.13	0^a	0.065
$r_5r_6{}^c$	0	0.0	2.2				

[a] In the limiting product- and reactant-like transition state, one of the O—H groups in **1** and **2** is replaced by C═C or C—C—H$^+$. Since no hydrogen bonds are formed to hydrocarbons, the corresponding force constants were assigned the value zero. [b] $F_\beta = 0.2$. [c] Interaction force constant.

Table III. Vibration Frequencies (cm^{-1}) Calculated from Models for H_2O, H_3O^+, C═C, $^+$C—C—H, and a Proton-Transfer Transition State ($z = 0.5$)

H_3O^+	H freq	D^a freq	H_2O	H freq	D^a freq	TS^b	H freq	D^a freq
ν_1 (a)	2840	2020	ν_1	3355	2425	$\nu_L{}^\ddagger$	655i	4751
ν_3 (e)	2540	1860	ν_3	3550	2605	$\nu_R{}^\ddagger$	510^c	460^c
						ν_{R_1}	3090	2265
ν_2 (a)	1140	860	ν_2	1645	1200	ν_{R_1}	3070	2210
ν_4 (e)	1630	1180				ν_{R_7}	985	980
				715	530			
ν_L (a)	580	410	ν_L	710	500	ν_{φ_1}	1570	1150
(e)	610	435		645	470	$\nu_{\varphi_{10}}$	1200	865
						ν_φ	1130	820
C═C			$^+$C—C—H					
							770	600^c
ν_s	1085	1085	ν_s	2900	2090	ν_L	695	510
			ν_b (e)	1240	925		615	410

[a] Solvating hydrogens are not isotopically substituted. [b] $\nu_R{}^\ddagger$ and $\nu_L{}^\ddagger$ denote the real and imaginary stretching modes associated with O--H--C. Otherwise, subscripts for ν refer to **3**, except that ν_L denotes librations. [c] $\nu_R{}^\ddagger$ and the 600-cm^{-1} librational mode are strongly coupled in the deuterium transition state.

the primary isotope effect $(k_H/k_D)_I$ is particularly sensitive to the extent of proton tunneling and the choice of the maximum value, F_β, for the O---H---C bending force constant. The value of $F_\beta = 0.2$ used here is smaller than that derived, by analogy, from the bending force constants of the bihalide ions[16] ($F_\beta \sim 0.35$). The lower value gives better agreement with observed isotope effects and is consistent with the net positive charge in transition state **3**.

The dependence of both the bending force constants and the stretch–stretch interaction force constant associated with the O---H---C unit upon transition state structure was handled in the same manner as before,[16] save that the force constants were maximized when the stretching force constants of the partial bonds to hydrogen were equal ($f_{r_5} = f_{r_6}$), rather than when the partial bond orders were equal ($z = (1 - z) = 0.5$).

Limiting values of the transition state force constants, as $z \rightarrow 0$ or 1, are shown in Table II. The corresponding frequencies are listed in Table III. The frequencies were derived by the Wilson FG matrix method,[22] and isotope effects upon rates and equilibria were calculated in the usual manner[23] using the Redlich–Teller product rule[22] and the first two expansion terms of Bell's correction for proton tunneling.[24]

Results and Discussion

An important assumption in the treatment of solvent isotope effects outlined in the introduction is that the effect of substitution at one isotopic position in a molecule or transition state is independent of that at any other. For symmetrical species, such as H_2O and H_3O^+, this implies that isotopic disproportionation equilibria should be statistically controlled and conform to the "rule of the geometric mean" or RGM.[4,5,25] Thus, for water, the ideal value of the equilibrium constant K_1 is 4.0.

$$H_2O + D_2O \rightleftharpoons 2HDO \qquad K_1$$

In practice it is now established that the rule of the mean is not exactly obeyed,[5,26–36] and one object of

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(22) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.

(23) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

(24) R. P. Bell, *Trans. Faraday Soc.*, **55**, 1 (1959); "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(25) J. Bigeleisen, *J. Chem. Phys.*, **23**, 2264 (1955); **28**, 694 (1958).

(26) P. Salomaa, *Acta Chem. Scand.*, **23**, 2095 (1969).

(27) M. Wolfsberg, *J. Chem. Phys.*, **50**, 1484 (1969).

(28) J. R. Hulston, *ibid.*, **50**, 1483 (1969).

(29) J. W. Pyper, R. S. Newbury, and G. W. Barton, Jr., *ibid.*, **46**, 2253 (1967); L. Friedman and V. J. Shiner, Jr., *ibid.*, **44**, 4639 (1966).

(30) J. Bigeleisen and P. Goldstein, *Z. Naturforsch. A*, **18**, 205 (1963).

(31) A. J. Kresge and Y. Chiang, *J. Chem. Phys.*, **49**, 1439 (1968).

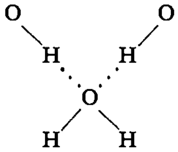
(32) V. Gold, *Trans. Faraday Soc.*, **64**, 2770 (1968).

(33) W. J. Albery and M. H. Davies, *ibid.*, **65**, 1059 (1969).

the present work was to use a combination of calculations and experiment to obtain practical estimates of the effect of deviations upon currently used simple treatments of solvent isotope effects.

Water. For water the value of K_1 may be calculated from the partition function ratio $4Q_{HDO}^2/Q_{H_2O}Q_{D_2O}$, in which the Q's are partition functions, exclusive of symmetry numbers, for the isotopic water species, and the factor 4 arises from the product of symmetry numbers for H_2O and D_2O. Calculations for H_2O in the gas phase, assuming free rotation and using a harmonic force field, give $K_1 = 3.87$. This value may be compared with the best results of anharmonic calculations, 3.72[28] and 3.85,[27] and the experimental values[29] of 3.74 and 3.76 (all at 25°). In the liquid, a harmonic calculation based on model **1** gives $K_1 = 3.91$. Although no precise direct measurements have been made for the liquid, the vapor pressures of H_2O, D_2O, and HDO conform closely to the rule of the mean,[37] so that the same value for liquid and vapor may sensibly be used. Here the value of 3.76 has been taken (*cf.* ref 26).

It may be objected that for liquid water **1** does not provide an adequate model. However, for the partially hydrogen-bonded species,[20] **4** and **5**, the calculations give $K_1 = 3.90$ and 4.02, respectively. For **5**, there is a slight modification of the treatment insofar as there are two species, HDO and HDO′, with hydrogen and deuterium atoms, respectively, bound, but in this case K_1 is simply given by an effective equilibrium constant expressing the total concentration of HDO species relative to the concentrations of H_2O and D_2O: $(\Sigma[HDO])^2/[H_2O][D_2O] = (Q_{HDO} + Q_{HDO'})^2/Q_{H_2O}Q_{D_2O}$. Thus, deviations from the RGM are not drastically different from those of model **1**, and when this is true it is not hard to show that K_1 for water considered as a mixture of species must be close to K_1 for the dominant component, which at 25° seems likely to be the fully hydrogen-bonded water[20] represented by **1**.



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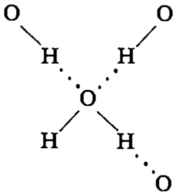

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It is evident that for H_2O the calculations consistently underestimate deviations from the RGM.[38] However, the calculated deviations have the correct direction and order of magnitude, and in what follows we have used calculations and experiment hand in hand to interpolate realistic or "practical" deviations for transition states and other species for which direct experimental measurements are lacking.

Bernstein's Rules. In comparing deviations from the rule of the mean from molecule to molecule, and between calculations and experiment, a convenient formalism is offered by Bernstein's rules.[30,39] Bernstein defined an additive property of a molecule as one which could be expressed in terms of a constant contribution from each atom plus an interaction term for each atomic pair. For such a property, P, of H_2O, D_2O, and HDO, the following relationship is implied

$$2P_{HDO} = P_{H_2O} + P_{D_2O} + \Delta_{HD}$$

where $\Delta_{HD} = 2p_{HD} - p_{HH} - p_{DD}$, and p_{HD}, p_{HH}, and p_{DD} represent the interaction terms between pairs of isotopic hydrogens. If we identify ln Q with P, where Q is again a partition function exclusive of symmetry numbers, we have

$$\Delta_{HD} = 2 \ln Q_{HDO} - \ln Q_{H_2O} - \ln Q_{D_2O}$$

and since we are dealing with products and ratios of partition functions, we may conveniently define a parameter δ_{HDO} exponentially related to Δ_{HD} and equal to $-\Delta_{HD}$ in the limit that δ_{HDO} is small (which is normally the case).

$$1 - \delta_{HDO} = e^{\Delta_{HD}} = Q_{HDO}^2/Q_{H_2O}Q_{D_2O}$$

Clearly $\delta_{HDO} = 1 - K_1/4$ and provides a measure of the deviation of water from the rule of the mean.

Calculated values of δ_{HDO} together with K_1 and Q_{D_2O}/Q_{H_2O} are listed in Table IV. Also shown are the corresponding values for H_2O, T_2O, and THO, and D_2O, T_2O, and DTO, which are of importance in connection with measurements involving tritium tracers.

Table IV. Calculated Deviations from the Rule of the Mean for Isotopic Water and Hydronium Ion Species

	L = H, M = D	L = H, M = T	L = D, M = T
Q_{M_2O}/Q_{L_2O}	1436.6	38912	27.086
K_1	3.915	3.826	3.984
δ_{LMO}	0.0214	0.0434	0.0041
$Q_{M_3O^+}/Q_{L_3O^+}$	18160	157560	86.763
K_2	25.87	24.70	26.77
K_3	25.89	24.75	26.77
$\delta_{L_2MO^+}$	0.0141	0.0292	0.0028
$\delta_{M_2LO^+}$	0.0139	0.0286	0.0028
L^a	8.991	23.73	2.640

[a] L is the equilibrium constant for $2M_3O^+ + 3L_2O \rightleftharpoons 2L_3O^+ + 3M_2O$ and is not to be confused with L, which conventionally denotes an unspecified hydrogen isotope.

Bernstein's rules are readily generalized to molecules with more than two hydrogens. For isotopic modifications XH_mD_{n-m} of the hydride XH_n, Δ_{HD} for an additive property P is given by $n - 1$ relations of the form

$$P_{XH_mD_{n-m}} = (m/n)P_{XH_n} + [(n - m)/n]P_{XD_n} + [m(n - m)/2]\Delta_{HD}$$

The validity of applying the rules to isotopic partition functions is considered further below.

A Simple Interpretation of Deviations from the Rule of the Mean. Bigeleisen and Goldstein[30] have pointed out that deviations from the RGM for harmonic zero-point energies of isotopic hydrides of the type XH_n

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(34) M. Wolfsberg, *Z. Naturforsch. A*, **18**, 216 (1963); J. Bigeleisen, R. E. Weston, Jr., and M. Wolfsberg, *ibid.*, *A*, **18**, 210 (1963); J. Bigeleisen and T. Ishida, *J. Chem. Phys.*, **48**, 1311 (1968); T. Ishida, W. Spindel, and J. Bigeleisen, *Advan. Chem. Ser.*, No. **89**, 192 (1969).

(35) J. W. Pyper, R. S. Newbury, and G. W. Barton, Jr., *J. Chem. Phys.*, **47**, 1179 (1967).

(36) J. W. Pyper and R. S. Newbury, *ibid.*, **52**, 1966 (1970).

(37) L. Merlivat, R. Botter, and G. Nief, *J. Chim. Phys. Physicochim. Biol.*, **60**, 56 (1963).

(38) Only a small part of the difference is due to the use of observed rather than zero-order frequencies; *e.g.*, our value of $K_1 = 3.87$ for H_2O in the gas phase compares with $K_1 = 3.84$ calculated from zero-order frequencies.[27]

(39) H. J. Bernstein, *J. Chem. Phys.*, **20**, 263 (1952).

derive principally from bending modes, in which the motion of the hydrogens is strongly correlated. This suggests that the zero-point energy of XH_n should be written in the approximate form

$$\mathrm{ZPE} = a + 2b\mu_{\mathrm{H}}^{1/2} + c(\mu_{\mathrm{H}} + \mu_{\mathrm{H}})^{1/2}$$

where μ_{H} is the reciprocal mass of hydrogen and a, b, and c are constants. The first two terms of this expression are the usual zero-order approximation for hydrogen zero-point energy, and the third term takes account of the H–X–H bending vibrations, with the assumption that the mass of X may be neglected and that no interaction with other vibrations occurs.[40] If this expression is applied specifically to XH_2, the zero-point energies for XD_2 and XHD may be written as follows

$$\mathrm{ZPE}_{\mathrm{XD_2}} = a + 2b\mu_{\mathrm{D}}^{1/2} + c(\mu_{\mathrm{D}} + \mu_{\mathrm{D}})^{1/2}$$

$$\mathrm{ZPE}_{\mathrm{XHD}} = a + b(\mu_{\mathrm{H}}^{1/2} + \mu_{\mathrm{D}}^{1/2}) + c(\mu_{\mathrm{H}} + \mu_{\mathrm{D}})^{1/2}$$

Assuming that zero-point energy is an additive property in Bernstein's sense, these relations may be combined to yield a value for Δ_{HD} which may readily be shown to apply not only to XH_2 but to XH_3 and higher hydrides also.

$$\Delta_{\mathrm{HD}} = (c/kT)[2(\mu_{\mathrm{H}} + \mu_{\mathrm{D}})^{1/2} - (2\mu_{\mathrm{H}})^{1/2} - (2\mu_{\mathrm{D}})^{1/2}]$$

It is apparent that on this interpretation only the H–X–H bending vibrations contribute to Δ_{HD}.[41] The interpretation may be tested by writing Δ_{HT}, the Bernstein parameter for zero-point energy changes accompanying substitution of tritium. When Δ_{HT} and Δ_{HD} are compared for the same molecule $\Delta_{\mathrm{HT}}/\Delta_{\mathrm{HD}}$ is given by

$$\frac{\Delta_{\mathrm{HT}}}{\Delta_{\mathrm{HD}}} = \frac{2(\mu_{\mathrm{H}} + \mu_{\mathrm{T}})^{1/2} - (2\mu_{\mathrm{H}})^{1/2} - (2\mu_{\mathrm{T}})^{1/2}}{2(\mu_{\mathrm{H}} + \mu_{\mathrm{D}})^{1/2} - (2\mu_{\mathrm{H}})^{1/2} - (2\mu_{\mathrm{D}})^{1/2}}$$

and is predicted to be independent of the molecule considered. A similar independence is expected of $\Delta_{\mathrm{HD}}/\Delta_{\mathrm{DT}}$ in a comparison of H–D and D–T isotope exchange, and substitution of the masses of H, D, and T leads to the values $\Delta_{\mathrm{HT}}/\Delta_{\mathrm{HD}} = 2.23$ and $\Delta_{\mathrm{HD}}/\Delta_{\mathrm{DT}} = 3.81$.

Harmonic calculations were carried out for the molecules NH_3, CH_4, CH_2Br_2, CH_3Br, H_2O (gas and liquid models), and H_3O^+ (hydrated and unhydrated) and gave average values of $\Delta_{\mathrm{HT}}/\Delta_{\mathrm{HD}} = 2.14$ and $\Delta_{\mathrm{HD}}/\Delta_{\mathrm{DT}} = 3.64$, with standard deviations of 0.08 and 0.17, respectively.[42] The reasonable constancy of these values and satisfactory agreement with those predicted supports the qualitative validity of this simple interpretation.

Deviations from the Rule of the Mean for Tritium. The constancy of $\Delta_{\mathrm{HT}}/\Delta_{\mathrm{HD}}$ and $\Delta_{\mathrm{HD}}/\Delta_{\mathrm{DT}}$ suggests a way of realistically assessing deviations from the rule of the mean for exchange of tritium. Because Δ is small, $\delta \sim -\Delta$, and since zero-point energy makes a dominant contribution to differences in isotopic partition function ratios, we might expect that $\delta_{\mathrm{HT}}/\delta_{\mathrm{HD}}$ and $\delta_{\mathrm{HD}}/\delta_{\mathrm{DT}}$, where the δ's refer to complete partition functions, will also be constant from molecule to molecule. In fact, calculations for the molecules listed above gives $\delta_{\mathrm{HT}}/\delta_{\mathrm{HD}} = 2.02$ and $\delta_{\mathrm{HD}}/\delta_{\mathrm{DT}} = 5.35$, with standard deviations of 0.04 and 0.25. Therefore, we have combined the calculated ratios of $\delta_{\mathrm{HTO}}/\delta_{\mathrm{HDO}}$ and $\delta_{\mathrm{HDO}}/\delta_{\mathrm{DTO}}$ with the *experimental* value of δ_{HDO} to obtain practical values of δ_{HTO} and δ_{DTO} for water. These values, together with the derived values of K_1 for HTO and DTO and the corresponding experimental value for HDO are shown in Table V.

Table V. Experimental and Practical Values for Deviations from the Rule of the Mean for H_2O and H_3O^+

	H_2O		$H_3O^{+\,a}$	
Isotopes	K_1	δ	K_2, K_3	δ
H, D	3.76	0.06	24.6	0.031
H, T[b]	3.52	0.12	22.2	0.063
D, T[b]	3.96	0.011	26.45	0.006

[a] Values for ammonia in the gas phase. [b] Values for H, T and D, T fractionation were interpolated in the manner described in the text.

Despite its shortcomings, in default of direct measurements, this procedure appears to offer a reasonable method for estimating experimentally based values of δ_{HT} and δ_{DT}.

Fractionation Factors. Experimentally, deviations from the rule of the mean for liquid water are revealed by the dependence of fractionation factors upon the isotopic composition of the solvent.[31–33] A fractionation factor, ϕ, measures the D/H ratio at an exchangeable position in a solute relative to that in the solvent;[43] for a solute X–H

$$\phi = \frac{[\mathrm{X-D}]}{[\mathrm{X-H}]}\frac{(1-x)}{x}$$

where x is the atom fraction of deuterium in the water. For fractionation of a single hydrogen site, deviations from the RGM are confined to the solvent and are reflected in the dependence of ϕ upon x.

Extreme values of ϕ are found when the solvent composition approaches pure H_2O or pure D_2O. These are conveniently denoted ϕ_0 and ϕ_∞.

$$\lim_{\mathrm{D/H}\to 0} \phi = \phi_0 = \frac{Q_{\mathrm{X-D}}\,Q_{\mathrm{H_2O}}}{Q_{\mathrm{X-H}}\,Q_{\mathrm{DHO}}}$$

$$\lim_{\mathrm{D/H}\to \infty} \phi = \phi_\infty = \frac{Q_{\mathrm{X-D}}\,Q_{\mathrm{HDO}}}{Q_{\mathrm{X-H}}\,Q_{\mathrm{D_2O}}}$$

As pointed out by Gold,[32] the dependence of ϕ upon x is usefully expressed in terms of the ratio $\phi_{\mathrm{rel}} = \phi/\phi_0$, and in Figure 1 $(1.0 - \phi_{\mathrm{rel}})$ is shown plotted against x (*cf.* ref 32 and 33). The extreme value of $1.0 - \phi_{\mathrm{rel}}$ at $x = 1$, given by $1.0 - \phi_\infty/\phi_0$, represents the maximum error that can be incurred in measurement of the fractionation factor by neglect of deviations from the RGM. Moreover, since

$$\phi_\infty/\phi_0 = Q_{\mathrm{HDO}}^2/Q_{\mathrm{H_2O}}Q_{\mathrm{D_2O}}$$

it follows that

$$1.0 - \phi_\infty/\phi_0 = \delta_{\mathrm{HDO}} = 0.06$$

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(40) Including the mass of X this term becomes $c[2\mu_{\mathrm{H}} + \mu_{\mathrm{X}}(1 - \cos\theta)]^{1/2}$, where θ is the H–X–H angle and the expression in brackets is the on-diagonal element of the G matrix for the bending coordinates. Even so, the mass dependence of the zero-point energy for bending is given exactly only in the case of a linear triatomic molecule XH_2.

(41) In H_2, correlation of H atoms occurs in the stretching mode.[30] For isotopic hydrogen molecules the expressions in this section are rigorously correct within the harmonic approximation.

(42) Serious discrepancies are found only for CH_2Br_2: $\Delta_{\mathrm{HT}}/\Delta_{\mathrm{HD}} = 2.41$ and $\Delta_{\mathrm{HD}}/\Delta_{\mathrm{DT}} = 2.83$.

(43) E. A. Halevi, F. A. Long, and M. A. Paul, *J. Amer. Chem. Soc.*, **83**, 305 (1961).

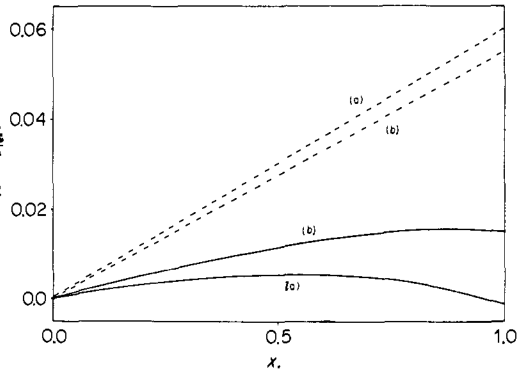

Figure 1. Plots of $1.0 - \phi_{rel}$ *vs.* x: (a) ----, for a single fractionating hydrogen; —, for H_3O^+ ($\phi_{rel} = l_{rel}$); (b) transition state ($z = 0.5$), ----, reacting hydrogen; —, nonreacting hydrogen.

The dependence of ϕ_{rel} upon x may thus be used to determine δ_{HDO} and K_1, and measurements by Kresge and Chiang[31] and by Gold[32] have given values consistent with those obtained by other methods.

A fractionation factor ϕ_T may also be derived from measurements of tritium fractionation in H_2O and D_2O.[44]

$$\phi_T = \frac{[X\text{–}T]\,[H_2O]}{[X\text{–}H][HTO]}\bigg/\frac{[X\text{–}T]\,[D_2O]}{[X\text{–}D][DTO]} = \frac{Q_{X\text{–}D}\,Q_{DTO}\,Q_{H_2O}}{Q_{X\text{–}H}\,Q_{HTO}\,Q_{D_2O}}$$

comparing ϕ_T and ϕ_0

$$\frac{\phi_T}{\phi_0} = \frac{Q_{DTO}\,Q_{HDO}}{Q_{HTO}\,Q_{D_2O}}$$

rewriting in terms of the Bernstein parameters, δ, for HDO, HTO, and DTO

$$\frac{\phi_T}{\phi_0} = \frac{(1 - \delta_{DTO})^{1/2}(1 - \delta_{HDO})^{1/2}}{(1 - \delta_{HTO})^{1/2}}$$

and from the values of δ listed in Table V, $\phi_T/\phi_0 = 1.028$

Thus, different methods of determination lead to different values for ϕ, with $\phi_T > \phi_0 > \phi_\infty$, and a possible range of nearly 10%. The calculated relative magnitudes of 1.0:1.064:1.094 for $\phi_\infty:\phi_0:\phi_T$ are in good qualitative agreement with experimental measurements for trimethoxybenzene[31,44] of 1.0:1.04:1.10.

The Hydronium Ion. Deviations from the rule of the mean for the hydronium ion may be expressed in the same manner as for water. Since H_3O^+ has three hydrogens, however, two independent isotopic disproportionation equilibria and associated Bernstein parameters may be written

$$D_3O^+ + 2H_3O^+ \rightleftharpoons 3H_2DO^+ \qquad K_2$$

$$2D_3O^+ + H_3O \rightleftharpoons 3D_2HO^+ \qquad K_3$$

$$1 - \delta_{H_2DO} = Q_{H_2DO^+}/Q_{H_3O^+}{}^{2/3} = K_2{}^{1/3}/3$$

$$1 - \delta_{D_2HO} = Q_{D_2HO^+}/Q_{H_3O^+}{}^{1/3} = K_3{}^{1/6}/3$$

where, as usual, symmetry numbers are omitted from the partition functions. Values of $K_2 = 25.87$ and $K_3 = 25.89$ were calculated from model **2** and are listed together with δ_{H_2DO} and δ_{D_2HO} in Table IV. For H_3O^+, the calculations allow a test of the applicability of Bernstein's rules, since for ln Q to be an additive property, we should have $\delta_{H_2DO} = \delta_{D_2HO}$ and $K_2 = K_3$. As seen from Table IV, the rules do apply to an excellent approximation (~2% in δ), a finding which is in line with earlier calculations of harmonic zero-point energies.[30,34] In this paper, it is further assumed that the rules apply to real as well as to harmonic partition functions.

No experimental measurements of deviations from the rule of the mean for H_3O^+ exist, but measurements for ammonia in the gas phase[35] yield values of $K_2 = 24.7$ and $K_3 = 24.5$. Since the intention of this work is to make realistic, though not necessarily exact, estimates of deviations from the RGM, it seemed sensible to take ammonia as a model for H_3O^+ in solution and adopt the practical values of $K_2 = K_3 = 24.6$.

The practical values of K_2, K_3, and δ for H_3O^+ are listed in Table V for fractionation of H and D, H and T, and D and T. Values of δ for tritium fractionation were derived in the same way as for H_2O by combining the experimental value of δ_{H_2DO} with the calculated values of δ_{H_2DO}, δ_{H_2TO}, and δ_{D_2TO} based on model **2** and listed in Table IV. The values may be used to investigate reactions of H_3O^+ involving all three isotopes of hydrogen.

Values of K_1, K_2, and K_3 from Table V can be used in conjunction with the equilibrium constant L (Table IV) to examine the dependence of l, the fractionation factor for the hydronium ion, upon the deuterium atom fraction, x, of the solvent water.[32] The value of l is given by

$$l = \left[\frac{3[D_3O^+] + 2[D_2HO^+] + [DH_2O^+]}{3[H_3O^+] + 2[DH_2O^+] + [D_2HO^+]}\right]\frac{(1 - x)}{x}$$

and as before, it is convenient to consider $l_{rel} = l/l_0$, where

$$l_0 = \lim_{D/H\to 0} l = \frac{Q_{H_2DO^+}Q_{H_2O}}{Q_{H_3O^+}Q_{HDO}}$$

Figure 1 shows a plot of $1.0 - l_{rel}$ *vs.* x, and it may be noted that at $x = 1$, $l_{rel} = l_\infty/l_0$, where

$$l_\infty = \lim_{D/H\to\infty} l = \frac{Q_{D_3O^+}Q_{HDO}}{Q_{HD_2O^+}Q_{D_2O}}$$

Again, the maximum value of $1.0 - l_{rel}$ represents the greatest error introduced into measurements of l by neglect of deviations from the rule of the mean. This is so small (~0.5%) as to be beyond the limits of detection by existing experimental methods, and it is apparent that cancellation of deviations from the rule of the mean between H_3O^+ and H_2O is practically complete.

This is of importance in connection with the demonstration that measurable fractionation in the hydronium ion is confined to three equivalent hydrogens[19,21,45,46] (as has been assumed here), which was based on the observed identities of l_0, l_∞, and $L^{-1/6}$. Since, from Figure 1, $l_0 = l_\infty$ to better than 0.1%,[47] and within the accuracy of Bernstein's rules $L^{-1/3} = l_0 l_\infty$, it is reasonable to consider that the conclusion is not sensibly affected by the assumption made that the isotopic equilibria conform to the rule of the mean.

The Equilibrium Constant *L*. As noted above, force constants in model **2** for the hydronium ion were as-

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[44] A. J. Kresge, D. P. Onwood, and S. Slae, *J. Amer. Chem. Soc.*, **90**, 6982 (1968).

[45] A. J. Kresge and A. L. Allred, *ibid.*, **85**, 1541 (1963); V. Gold, *Proc. Chem. Soc.*, 141 (1963).

[46] V. Gold and B. M. Lowe, *J. Chem. Soc. A*, 936 (1967).

[47] $l_0 = l_\infty$ if Bernstein's rules are obeyed and $(1 - \delta_{HDO})^{1/2} = 1 - \delta_{H_2DO}$; *i.e.*, if $K_1{}^{1/2}/2 = K_2{}^{1/3}/3 = K_3{}^{1/3}/3$ (*cf.* ref 32).

Table VI. Calculated Isotope Effects for Proton Transfer with "Practical" Corrections[a]

z	$\frac{k^{H}(H_2O)}{k^{D}(H_2O)}$	$\frac{k^{H}(H_2O)}{k^{H}(D_2O)}$	$\frac{k_H}{k_D}$	$(1 - R_1) \times 10^2$	$(1 - R_2) \times 10^2$	$(1 - R_1^T) \times 10^2$	Swain exponent
0[b]	1.0	1.0	1.0	0	0	0	
0.125	3.10	0.946	2.95	0.5	0.3	1.3	1.440
0.25	4.70	0.864	4.16	2.3	0.4	3.9	1.441
0.375	6.27	0.788	5.16	4.4	0.8	6.9	1.429
0.5	6.08	0.730	4.69	5.5	1.2	8.5	1.429
0.625	4.40	0.681	3.18	5.8	1.6	8.9	1.441
0.75	2.81	0.634	1.89	5.7	2.4	8.9	1.448
0.875	1.75	0.566	1.06	6.0	2.9	9.1	1.450
1.0[c]	0.677	0.470	0.339	6.0	3.0	9.2	1.457

[a] $k^{H}(H_2O)/k^{H}(D_2O)$, R_1, R_2, and R_1^T are practical values, interpolated as described in the text. [b] Reactants. [c] Products.

signed to give agreement with the best experimental value[19,21] of 9.0 at 25° for the equilibrium constant, L, for fractionation of hydrogen and deuterium isotopes between H_3O^+ and H_2O

$$L = \frac{Q_{H_3O^+}{}^2 Q_{D_2O}{}^3}{Q_{D_3O^+}{}^2 Q_{H_2O}{}^3}$$

It was found that the calculations precisely reproduced the measured temperature dependence[21] of L in the range 0–50°.

Calculations were also made of the corresponding equilibrium constants for fractionation of H and T and of D and T

$$2T_3O^+ + 3H_2O \rightleftarrows 2H_3O^+ + 3T_2O$$

$$2T_3O^+ + 3D_2O \rightleftarrows 2D_3O^+ + 3T_2O$$

and their values are recorded in Table IV. From values of L(H,T) and L(H,D), the exponent of the Swain relation[48,49] between deuterium and tritium isotope effects was calculated as 1.442, in precise agreement with the accepted value. The agreement was much poorer (1.38–1.40) for individual isotopic partition function ratios, and it is apparent that the presence of H–O–H bending modes in these species causes deviations from the Swain relation[49] in much the same way as they cause deviations from the rule of the mean. The good agreement for the equilibrium constant L again stems from far-reaching cancellation of zero-point energy for bending modes between H_2O and H_3O^+.

No experimental measurements of L(H,T) have yet been reported, but the related value of the autoprotolysis constant for T_2O, $K_w(T_2O)$, has recently been measured.[50] Application of the Swain relation to the observed value of $K_w(H_2O)/K_w(T_2O) = 16.4$ gives $K_w(H_2O)/K_w(D_2O) = 7.0$, in good agreement with recent measurements,[49–51] which fall in the range 7.06–7.35.

Kinetic Isotope Effects. Kinetic isotope effects were calculated for the model proton-transfer reaction

$$H_3O^+ + C{=}C \longrightarrow [H_2O{-}{-}{-}H{-}{-}{-}C{=}C]^{\ddagger} \longrightarrow H_2O + H{-}C{-}C^+$$

where model **2** was used for the hydronium ion and model **3** for the transition state. Several independent isotope effects can be calculated, depending on the positions of isotopic substitution. These may be specified by a notation in which the transferred hydrogen is indicated by a superscript and the nonreacting hydrogens in parentheses, as in k^{H}(HDO). Primary and secondary isotope effects, $k^{H}(H_2O)/k^{D}(H_2O)$ and $k^{H}(H_2O)/k^{H}(D_2O)$, are listed in Table VI as a function of z, the partial H---C bond order, for transition states ranging in structure from reactant-like to product-like. Values for z = 0 and 1 correspond to reactants and products, respectively. Also shown are values of $k^{H}(H_2O)/k^{D}(D_2O)$, which are directly accessible experimentally and are abbreviated k_H/k_D.

The first point to be considered is the dependence of isotopic substitution at one position upon that at another. This may be expressed by the isotope effect ratios R_1 and R_2, where

$$\frac{k^{H}(H_2O)}{k^{D}(H_2O)} = R_1\frac{k^{H}(D_2O)}{k^{D}(D_2O)} \qquad \frac{k^{H}(H_2O)}{k^{H}(D_2O)} = R_1\frac{k^{D}(H_2O)}{k^{D}(D_2O)}$$

$$R_2 = \frac{[k^{H}(HDO)]^2}{k^{H}(H_2O)k^{H}(D_2O)}$$

R_1 measures the effect of deuterium substitution at the secondary position upon the primary isotope effect, and of substitution at the primary position upon the secondary isotope effect. R_2 is evidently analogous to K_1 for H_2O. We may anticipate that directly calculated values of R_1 and R_2 underestimate the interdependence of isotopic substitution. However, by application of Bernstein's rules it is possible to use R_1 and R_2 as a basis for interpolating a more realistic "practical" set of isotope effects.

Bernsteins's rules require minor modification for application to an unsymmetrical species such as a proton transfer transition state. However, we may define an additive property P in the usual way, and if we specify the isotopic composition of the transition state by a subscript of the type H_2O–H′, where the reacting hydrogen is distinguished by a prime, we may write with the normal assumptions

$$P_{H_2O\text{-}D'} + P_{D_2O\text{-}H'} = P_{H_2O\text{-}H'} + P_{D_2O\text{-}D'} + 2\Delta_{HD}'$$

and

$$2P_{HDO\text{-}H'} = P_{H_2O\text{-}H'} + P_{D_2O\text{-}H'} + \Delta_{HD}$$

where $\Delta_{HD}' = (p_{DH'} + p_{HD'} - p_{DD'} - p_{HH'})$ and $\Delta_{HD} = (2p_{HD} - p_{HH} - p_{DD})$, and the contribution of interactions between nonreacting hydrogens, H–H, is denoted by p_{HH}, and between a reacting and nonreacting hydrogen, H–H′, by $p_{HH'}$. It may be noted that $\Delta_{HD'}$ involves only H–H′ interactions and Δ_{HD} only H–H interactions.

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(48) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **80**, 5885 (1958); E. S. Lewis and J. K. Robinson, *ibid.*, **90**, 4337 (1968); J. R. Jones, *Trans. Faraday Soc.*, **65**, 2138 (1969).

(49) J. Bigeleisen, "Tritium in the Physical and Biological Sciences," IAEA, Vienna, Vol. 1, 1962, p 161.

(50) M. Goldblatt and W. M. Jones, *J. Chem. Phys.*, **51**, 1881 (1969).

(51) A. K. Covington, R. A. Robinson and R. G. Bates, *J. Phys. Chem.*, **70**, 3820 (1966); L. Pentz and E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 6931 (1967).

If ln Q is an additive property of the transition state, we may define parameters δ_1 and δ_2 as follows

$$(1 - \delta_1)^2 = e^{2\Delta_{HD}} = \frac{Q_{H_2O-D'}Q_{D_2O-H'}}{Q_{H_2O-H'}Q_{D_2O-D'}}$$

$$(1 - \delta_2) = e^{\Delta_{HD}} = \frac{Q^2{}_{HDO-H'}}{Q_{H_2O-H'}Q_{D_2O-H'}} = \frac{Q^2{}_{HDO-D'}}{Q_{H_2O-D'}Q_{D_2O-D'}}$$

where δ_1 and δ_2 are clearly analogous to the Bernstein parameters δ_{HDO} and δ_{H_2DO} defined for H_2O and H_3O^+. The applicability of the rules is verified by lack of dependence of calculated values of δ_2 upon the isotope in the primary position.

If R_1 and R_2 are written in terms of partition functions for the reactants and transition state, substitution of δ_1, δ_2, and δ_{H_2DO} gives[52]

$$R_1 = \left(\frac{1 - \delta_{H_2DO}}{1 - \delta_1}\right)^2 \qquad R_2 = \frac{1 - \delta_2}{1 - \delta_{H_2DO}}$$

The virtue of this representation is that in the reactants ($z = 0$), $\delta_1 = \delta_2 = \delta_{H_2DO}$, while in the products ($z = 1$), in which H–H′ interactions are absent and H–H interactions are those of the water molecule, $\delta_1 = 0$ and $\delta_2 = \delta_{HDO}$. Since the calculated values of δ_1 and δ_2 for all transition states fall between their limiting values in reactants and products, they may reasonably be used as a basis for interpolating *practical* values of δ_1 and δ_2 from the practical and experimental values of δ_{HDO} and δ_{H_2DO} listed in Table V.[53]

The practical values of δ_1 and δ_2 may in turn be used to calculate the practical values of R_1 and R_2 listed as $1.0 - R_1$ and $1.0 - R_2$ in Table VI. These values of R_1 and R_2 may be used in conjunction with the calculated primary and solvent isotope effects $k^H(H_2O)/k^D(H_2O)$ and k_H/k_D to derive realistically related values for all other deuterium isotope effects, of which the secondary effects, $k^H(H_2O)/k^H(D_2O)$, are shown in Table VI.

Calculations were also made of isotope effects for transfer of tritium. The effect of tritium upon deuterium substitution of the nonreacting hydrogens is given by R_1^T, where

$$k^H(H_2O)/k^H(D_2O) = R_1^T k^T(H_2O)/k^T(D_2O)$$

and R_1^T is analogous to R_1 except that deuterium at the reacting position is replaced by tritium. From the calculated values of R_1^T, practical values may be derived in a manner sufficiently similar to that for R_1 that it need not be detailed.[54] The practical values are listed in Table VI and may be used to derive practical estimates of the secondary deuterium isotope effect upon tritium transfer.

The Effect of Supplementary Isotopic Substitution. As can be seen from Table VI, all values of R_1 and R_1^T are <1.0. This means that D or T isotopic substitution at the primary position increases the secondary isotope effect, and at the secondary position increases the primary isotope effect. This result is in line with Bigeleisen's rule that zero-point energy changes accompanying substitution at one position in a molecule increase with the extent of deuterium substitution at other positions.[30] The magnitude of this effect depends on the degree of interaction between the isotopic positions, which is largely determined by the size of the bending force constant between the bonds. Since, for proton transfer from a hydronium ion, interaction between reacting and nonreacting hydrogens decreases in going to the transition state (and, more specifically, the force constant f_{ϕ_2} in **3** decreases), the effect is greater in the reactants, with the result that kinetic isotope effects (k_H/k_D) are increased. This should generally be the case for deuterium substitution at an atom *from* which hydrogen is transferred. For substitution at an atom *to* which hydrogen is transferred the converse is true, and the isotope effect should be diminished.

These "rules" include the reacting hydrogen itself, and they should apply to both kinetics and equilibria. The decrease in fractionation factor for a single exchangeable hydrogen with increasing deuterium content of water is one example of their application. The effect of tritium substitution is in the same direction but greater in magnitude than that of deuterium, as witnessed by the smaller values of R_1^T than R_1.

Tests of Experimental Methods. We now have in hand a set of deuterium and tritium isotope effects which may be used as a realistic basis for testing the effectiveness of current methods in making the separation of primary and secondary isotope effects, $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$, outlined in the introduction.

Experimentally, independence of isotopic substitution is normally assumed. This means that the kinetic dependence of a proton transfer reaction upon the deuterium atom fraction x of a mixed H_2O–D_2O solvent may be written[5,8]

$$k_x/k_H = (1 - x + x\phi_1)(1 - x + x\phi_2)^2/(1 - x + xl)^3 \quad (1)$$

where k_x and k_H are rate constants for the mixture and pure H_2O, and l, ϕ_1, and ϕ_2 are composition-independent fractionation factors for H_3O^+ and the reacting and nonreacting hydrogens in the transition state. Since $(k_H/k_D)_I = l/\phi_1$ and $(k_H/k_D)_{II} = l^2/\phi_2^2$, the separation of primary and secondary isotope effects reduces to the determination of ϕ_1 and ϕ_2.

One relation between ϕ_1 and ϕ_2 is given by the solvent isotope effect for the reaction in pure D_2O

$$k_D/k_H = \phi_1\phi_2^2/l^3$$

A second relation may be obtained by one of two methods: (a) $\phi_1 = (l^3k_D/k_H)/\phi_2^2$ is substituted into the expression for k_x/k_H and ϕ_2 is adjusted to give the best fit of calculated to experimental values[5,8] and (b) ϕ_1 is determined independently by measuring the D/H ratio in the products as a function of x. The latter method is feasible when the reacting hydrogen is transferred to a nonexchangeable position in the products.[5,14]

The effectiveness of method a can be examined by evaluating k_x/k_H as a function of x from the calculated set of practical isotope effects, and then obtaining ϕ_1 and ϕ_2 from k_H/k_D and a best fit of eq 1 to the calculated values in the manner described. Values of $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$ obtained in this way are shown in Table VII in the column headed "RGM." Method b can be investigated by using the calculated isotope effects to

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(52) It is assumed that $\delta_{H_2DO} = \delta_{HD_2O}$, as required by Bernstein's rules.

(53) In fact it was assumed that $\delta_1/\delta_{H_2DO} = \delta_1'/\delta_{H_2DO}'$ and $(\delta_2 - \delta_{H_2DO})/(\delta_{HDO} - \delta_{H_2DO}) = (\delta_2' - \delta_{H_2DO}')/(\delta_{HDO}' - \delta_{H_2DO}')$, where calculated values of δ are distinguished from practical and experimental values by primes.

(54) The further assumption that $p_{HT'} = p_{TH'}$ is required. The validity of this is borne out by the fact that calculated values of R_1^T/R_1 fall within 2% of values predicted by assuming that $\delta_1/\delta_1^T = \delta_{H_2DO}/\delta_{H_2TO}$.

Table VII. Primary and Secondary Isotope Effects Derived by Different Methods

	Primary			Secondary				
z	From k_H/k_T	From ϕ_0	RGM[a]	$\frac{k^T(H_2O)}{k^T(D_2O)}$	From ϕ_0	RGM[a]	α^b (k_H/k_T)	α^b (RGM)
0[c]	1.0	1.0	1.0	1.0	1.0	1.0	0.0	0.0
0.125	3.10	3.10	3.13	0.958	0.950	0.942	0.06	0.08
0.25	4.70	4.70	4.84	0.899	0.884	0.859	0.15	0.21
0.375	6.17	6.27	6.58	0.846	0.824	0.784	0.23	0.33
0.5	5.98	6.08	6.45	0.797	0.772	0.728	0.31	0.43
0.625	4.39	4.40	4.68	0.748	0.723	0.680	0.40	0.53
0.75	2.82	2.81	2.98	0.696	0.672	0.632	0.50	0.63
0.875	1.75	1.75	1.87	0.625	0.604	0.563	0.64	0.78
1.0[d]	0.675	0.677	0.842	0.511	0.500	0.403	0.92	e

[a] From a best fit to calculated values of k_z/k_H. [b] $\alpha = \log (k_H/k_D)_{II}/2 \log l$. This definition makes α more sensitive to the method of measurement than the secondary isotope effects themselves. [c] Reactants. [d] Products. For a limiting product-like transition state, one of the hydrogen-bonding O–H groups of model **1** is replaced by H–C–C$^+$, to which no hydrogen bond is formed. Consequently, the calculated value of $(k_H/k_D)_{II}$ is larger and α is smaller than for the products themselves. [e] The RGM method leads to poor values of the isotope effects and $\alpha = 1.24$ for the products. This does not occur normally for equilibria involving H_3O^+ because l is not treated as an unknown.

determine ϕ_1 as a function of x. The limits ϕ_1^0 and ϕ_1^∞, which occur at $x = 0$ and $x = 1$, should represent extreme values obtainable by method b. Table VII lists primary and secondary isotope effects derived from ϕ_1^0 and k_H/k_D, and Figure 1 shows the dependence of $1.0 - \phi_1/\phi_1^0$ upon x for a transition state with the H---C bond order $z = 0.5$ (it may be noted that $\phi_1^\infty/\phi_1^0 = R_1 l_\infty/l_0$).

A third method[10,44] (c) of obtaining $(k_H/k_D)_{II}$ is by measuring tritium transfer rates in H_2O and D_2O. These values are given by the calculated product $R_1{}^T k^H(H_2O)/k^H(D_2O)$ and are also shown in Table VII. In some cases a primary isotope effect can be found from the Swain relation, and Table VII lists calculated values of $[k^H(H_2O)/k^T(H_2O)]^{1/1.442}$ for $(k_H/k_D)_I$.

Comparing the different methods, we may note that $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$ derived from ϕ_1^0 are very close to the calculated values of $k^H(H_2O)/k^D(H_2O)$ and $k^H(H_2O)/k^H(D_2O)$ (Table VI). Although they are not shown, values from ϕ_1^∞ were similarly close to $k^H(D_2O)/k^D(D_2O)$ and $k^D(H_2O)/k^D(D_2O)$. The reason for this is that deviations from the rule of the mean for the nonreacting hydrogens in the transition state are largely canceled with those of the hydronium ion. This is illustrated by comparison of the dependences of ϕ_2 and l upon x shown in Figure 1. The cancellation is not as great as between H_2O and H_3O^+ as can best be understood by deriving the relation between the limiting values of ϕ_2 and l as $x \rightarrow 0$ and 1, $\phi_2^\infty/\phi_2^0 = (l_\infty/l_0)(R_1^{1/2}/R_2)$, and noting from Table VI that for reactant-like transition states R_1 decreases more sharply with the extent of proton transfer than does R_2, so that $R_1^{1/2}/R_2$ is consistently less than unity. (The sharp decrease in R_1 occurs because the interaction between primary and secondary hydrogens is effectively removed ($\delta_1 \rightarrow 0$) by a small degree of O–H$^+$ bond breaking.) Nonetheless, the cancellation is sufficiently complete to suggest that careful measurements of ϕ_1 as a function of x by method b may yield quite precise values for the different isotope effects. So far, no variation of ϕ_1 with x has been detected.[5,14]

The "best fit" method (a) gives isotope effects close to those from ϕ_∞, with $(k_H/k_D)_I$ slightly greater and $(k_H/k_D)_{II}$ slightly smaller. As would be expected, the weakest secondary isotope effects are from measurements with tritium, by method c. Values of $(k_H/k_D)_I$ are close to $k^H(H_2O)/k^D(H_2O)$ since, according to the calculations, the Swain relation between primary isotope effects for deuterium and tritium was quite well obeyed (Table VI).

We may conclude that different methods yield the following relative magnitudes of isotope effects: for $(k_H/k_D)_{II}$, (c) > (b) > (a); and for $(k_H/k_D)_I$, (a) > (b) and, usually, (b) > (c). However, the largest discrepancies are little more than 10% and differences may be masked by experimental errors. Values obtained experimentally by the different methods are compared in Table VIII.

Isotope Effects and Transition State Structure. The main conclusion of the above analysis must be that neglect of interdependence of isotopic substitution does not obscure the strong correlations between $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$ and the structure of the transition state, revealed both by the directly calculated isotope effects and by the derived values of Table VII. For a consistent method of determination, $(k_H/k_D)_{II}$ decreases monotonically with the degree of proton transfer in the transition state, and calculation of the parameter α defined by the relation

$$(k_H/k_D)_{II} = l^{2\alpha}$$

evidently provides a direct measure of transition state structure. Values of α obtained from extreme values of $(k_H/k_D)_{II}$ are shown in Table VII. Although α underestimates the order of the partial bond to the substrate, z, its trend is unambiguous, and it is only moderately sensitive to the experimental method of determination.

As z increases, $(k_H/k_D)_I$ also changes characteristically and passes through a maximum close to $z = 0.5$. This behavior has been predicted[16,23,17,55] and found[56] for primary isotope effects uncomplicated by the presence of large secondary effects. In the present case the maximum is clearly indicated by a plot of $(k_H/k_D)_I$ *vs.* $(k_H/k_D)_{II}$, as shown by the dashed curve in Figure 2. This correlation is open to experimental test, and in Figure 2 the measured values of $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$ from Table VIII are also plotted.

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(55) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(56) J. E. Dixon and T. C. Bruice, *J. Amer. Chem. Soc.*, **92**, 905 (1970); R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 194 (1970); A. F. Cockerill, *ibid.*, *B*, 964 (1967); D. J. Barnes and R. P. Bell, *Proc. Roy. Soc., Ser. A*, **318** 421 (1970); W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, Chapter 4 and references cited therein.

Table VIII. Experimental Measurements of Primary and Secondary Solvent Isotope Effects

Substrate, acid, temp, °C	k_H/k_D	Primary[a] a	Primary[a] b or c*	Secondary[a] a	Secondary[a] b or c*	σ[b]
Diazoacetic acid anion, buffers,[e] 25	2.3		2.9		0.79	
2-Dichloromethylene-1,3-dioxolane,[f] HCl, 25	2.55	3.7	3.6	0.69	0.71	0.0050
2-(4-Methoxyphenyl)propene,[g] H_2SO_4, 48.6	3.13	(4.4)[c]		(0.72)[c]		0.0011
Ethyl vinyl ether,[h] $HClO_4$, 26.7	2.95	4.6		0.65		0.0035
Ethyl vinyl ether,[i] $HClO_4$, 25	3.2		4.9		0.66	
2-Chloroethyl vinyl ether,[j] HCl, 25	2.52	4.0		0.63		0.0087
Cyanoketene dimethyl acetal,[k] $HClO_4$, 25	3.09	4.7		0.63		0.0024
Allylmercuric iodide,[l] $HClO_4$, 25	3.12	5.7	5.1	0.54	0.62	0.0187
Trimethoxybenzene,[m] $HClO_4$, 24.6			5.9*		0.59*	
Azulene-*1-t*,[n] $HClO_4$, 25			7.2		0.59	
Isobutenylmercuric iodide,[o] 25	2.50	4.2	4.7	0.60	0.54	0.0113
2,6-Dimethoxybenzeneboronic acid,[p] $HClO_4$, 60	1.73	(3.0)[d]		(0.58)[d]		0.0039
2,4-Dimethoxyphenylmercuric acetate,[q]	2.87	5.1		0.56		0.0020
2,3-Dihydropyran[r]	2.18	4.0		0.55		0.0110
2-Methyl-2-butene,[s] HNO_3, 30	1.22	2.3		0.54		0.0119
1-Methylcyclopentene-1,[s] HNO_3, 35.2	0.93	1.7		0.54		0.0131
Isobutylene,[t] $HClO_4$, 25	1.46	2.9	2.7, 2.7*	0.50	0.54	0.0028

[a] Headings indicate method of measurement: a, by best fit of calculated to observed values of k_x/k_H; b, from isotope fractionation in product; c, from rates of tritium transfer (indicated by an asterisk). [b] $\sigma = \{\Sigma^N[(k_x/k_H)_{obsd} - (k_x/k_H)_{calcd}]^2/N(N-1)\}^{1/2}$ for the "best fit" method (a), where N = number of measurements of k_x/k_H. [c] Not included in Figure 2 because of possibility of bisulfate catalysis: J. M. Williams, Jr., *Tetrahedron Lett.*, 4807 (1968). [d] Not included in Figure 2 because of high temperature. [e] M. M. Kreevoy and D. E. Konasewich, submitted for publication. [f] V. Gold and D. C. A. Waterman, *J. Chem. Soc. B*, 849 (1968), with $k_D/k_H = 0.3927$ and $k_H = 0.1008$. [g] J-C. Simandoux and B. Torck, *Tetrahedron Lett.*, 2971 (1967). [h] A. J. Kresge and Y. Chiang, *J. Chem. Soc. B*, 58 (1967). [i] M. Kreevoy and R. Eliason, *J. Phys. Chem.*, **72,** 1313 (1968). [j] P. Salomaa, A. Kankaanperä, and M. Lajunen, *Acta Chem. Scand.*, **20,** 1790 (1966). [k] V. Gold and D. C. A. Waterman, *J. Chem. Soc. B*, 839 (1968). [l] M. Kreevoy, P. J. Steinwand, and W. V. Kayser, *J. Amer. Chem. Soc.*, **88,** 124 (1966). [m] A. J. Kresge and Y. Chiang, *ibid.*, **89,** 4411 (1967); A. J. Kresge, D. P. Onwood, and S. Slae, *ibid.*, **90,** 6982 (1968); A. J. Kresge and Y. Chiang, *J. Chem. Phys.*, **49,** 1439 (1968); $(k_H/k_D)_I$ was derived in the manner described in these papers. [n] J. L. Longridge and F. A. Long, *J. Amer. Chem. Soc*, **89,** 1292 (1967), and references cited therein. Values of $(k_H/k_D)_I$ and $(k_H/k_D)_{II}$ were derived as described, but corrections for secondary isotope effects were applied, assuming that these were the same as for trimethoxybenzene. [o] M. M. Kreevoy and R. A. Landholm, *Int. J. Chem. Kinet.*, **1,** 157 (1969). [p] H. G. Kuivala and K. V. Nahabedian, *J. Amer. Chem. Soc.*, **83,** 2164 (1961). [q] A. J. Kresge and J. F. Brennan, unpublished data. [r] A. Kankaanperä, *Acta Chem. Scand.*, **23,** 1465 (1969). [s] E. L. Purlee and R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **78,** 5807 (1956). [t] V. Gold and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965), with $k_H/k_D = 1.46$ and $k_H = 2.74 \times 10^{-4}$ M^{-1} sec^{-1}.

Inspection of Figure 2 at first suggests that the distribution of experimental points is nearly random. Closer examination, however, indicates that this is principally true of results obtained by the best fit method, which are shown as open circles. As has been pointed out by Gold and Waterman,[57] this method is rather insensitive to the absolute values of the primary and secondary isotope effects, and it is likely that a number of the measurements lack the precision necessary in this application (*cf.* ref 5). Inspection of the more accurate results obtained by methods b and c, and shown as closed circles, reveals distinct evidence of an isotope maximum. Although further measurements will be required, this is a good preliminary demonstration of qualitative agreement between the calculations and experiment.

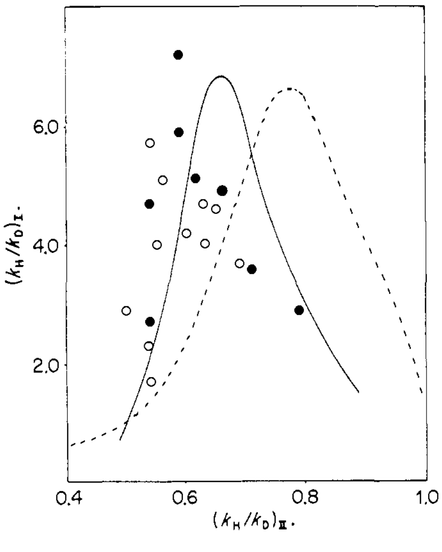
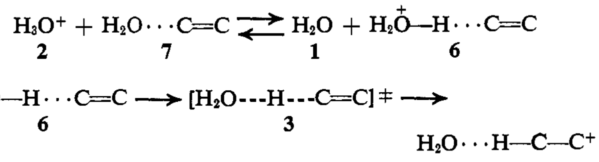


Figure 2. Plot of primary *vs.* secondary solvent isotope effects: ○, experimental, method a; ●, experimental, methods b and c; ----, calculated, Table VII; —calculated, Table IX.

The calculations also indicate a maximum in the variation of the overall "solvent" isotope effect $k^H(H_2O)/k^D(D_2O)$ (k_H/k_D in Table VI) with changes in transition state structure. This has been found experimentally from measurements of k_H/k_D as a function of reactivity for the hydration of a series of vinyl ethers and related substrates.[58] Because of the contribution from the secondary effect, the maximum is less pronounced than for the primary isotope effect alone.

Transfer Effects. A last factor that can be investigated by these calculations is the influence of "transfer" or medium effects[5,59] arising from fractionation of hydrogens other than those of the H_3O^+ unit. A possible source of such an effect is indicated by writing the model proton-transfer reaction as follows



$$\underset{\mathbf{2}}{H_3O^+} + \underset{\mathbf{7}}{H_2O\cdots C{=}C} \rightleftharpoons \underset{\mathbf{1}}{H_2O} + \underset{\mathbf{6}}{H_2\overset{+}{O}{-}H\cdots C{=}C}$$

$$\underset{\mathbf{6}}{H_2\overset{+}{O}{-}H\cdots C{=}C} \longrightarrow \underset{\mathbf{3}}{[H_2O{-}{-}{-}H{-}{-}{-}C{=}C]^{\ddagger}} \longrightarrow H_2O\cdots H{-}C{-}C^+$$

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(57) V. Gold and D. C. A. Waterman, *J. Chem. Soc. B*, 839 (1968).

(58) A. J. Kresge, D. S. Sagatys, and H. L. Chen, *J. Amer. Chem. Soc.*, **90,** 4174 (1968).

(59) D. M. Goodall and F. A. Long, *J. Amer. Chem. Soc.*, **90,** 238 (1968); V. Gold, *Trans. Faraday Soc.*, **64,** 2143 (1968).

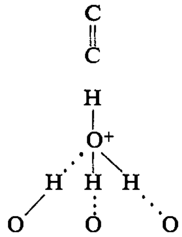
Table IX. Practical Isotope Effects with Preequilibrium Corrections

	Primary				Secondary			
z	k_H/k_D	RGM	ϕ_0	ϕ_∞	RGM	ϕ_0	ϕ_∞	α(RGM)
0[a]	0.694	0.780	0.753	0.751	0.889	0.922	0.925	0.16
0.125	1.67	1.95	1.92	1.94	0.859	0.870	0.861	0.21
0.25	2.46	3.08	3.00	3.07	0.799	0.819	0.800	0.31
0.375	3.48	4.74	4.56	4.75	0.733	0.762	0.732	0.42
0.5	4.53	6.82	6.40	6.76	0.665	0.709	0.671	0.56
0.625	4.09	6.49	6.21	6.57	0.631	0.660	0.623	0.63
0.75	2.42	4.13	3.95	4.20	0.585	0.611	0.576	0.73
0.875	1.16	2.15	2.07	2.20	0.539	0.559	0.527	0.84
1.0[b]	0.339	0.697	0.677	0.721	0.486	0.500	0.470	0.99

[a] Limiting reactant-like transition state. [b] Limiting product-like transition state *and* products.

Here, a preequilibrium is added in which a water molecule in the solvation shell of the substrate is replaced by H_3O^+.

This formulation follows naturally from considering the limiting reactant-like transition state as a hydronium ion with one of its solvating O—H groups replaced by the substrate C=C (model **6**), as indeed has been done throughout these calculations. Since in the reactants the hydronium ion must be fully solvated and the substrate completely surrounded by water molecules, a necessary preliminary to formation of the transition state is displacement of a water molecule adjacent to C=C (as in model **7**) by H_3O^+. This may be pictured as exchange of a solvating water molecule and C=C between the solvation shells of H_3O^+ and H_2O. As may be seen, all kinetic isotope effects calculated solely from consideration of transition state **3** and the hydronium ion (**2**) are modified by a transfer effect arising from the zero-point energy difference between the water in model **7** and in its fully solvated form.



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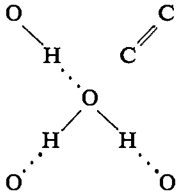

7

The isotope effect on going from model **7** to fully solvated water (model **1**) was calculated by assuming that no hydrogen bonds are formed to carbon, and that bending and stretching force constants associated with the carbon–oxygen "bond" are zero. This led to a reduction in the net value of k_H/k_D of about 8%. It will be noted that with this model there is no effect on the equilibrium isotope effect, since C=C in **6** is simply replaced by H—C—C$^+$, with no change in force constants in the water segment. There are, of course, other water molecules in the solvation shell of the substrate, but it was assumed that these are carried over unchanged into the transition state and product.

Since the preequilibrium process involves desolvation of H_3O^+, it was also considered that the limiting force constant for the reacting O–H$^+$ bond should be increased, and the value of 6.6 mdyn/Å appropriate to H_3O^+ in sulfur dioxide solution[20] was adopted. Values of k_x/k_H were evaluated using the previously calculated practical isotope effects modified by the fractionation associated with the preequilibrium. Primary and secondary isotope effects were then determined by the best fit method and by combination of ϕ_0 and ϕ_∞ with k_H/k_D in the manner described above.

From Table IX, in which $(k_H/k_D)_I$, $(k_H/k_D)_{II}$, and values of α are listed, it is apparent that there is no substantial change in the correlation of isotope effects with transition state structure, or even in the relative magnitudes of isotope effects derived by different methods. However, the transfer contribution does have the effect of reducing $(k_H/k_D)_{II}$ and increasing α. This is particularly noticeable for a limiting reactant-like transition state where the preequilibrium introduces a discontinuity with the reactants and α no longer reduces to zero. On the other hand, α does now approach unity for a limiting product-like transition state, which is not the case for calculations neglecting transfer where a discontinuity exists with the products (*cf.* Table VII footnote *d*).

The greater limiting O–H$^+$ force constant causes the primary isotope effect to reach its greatest value for a smaller degree of proton transfer. This factor and the decrease in secondary isotope effects, caused by the transfer contribution, combine to reduce the value of $(k_H/k_D)_{II}$ at which $(k_H/k_D)_I$ is a maximum, as is shown by the continuous curve in Figure 2. Interestingly, Figure 2 indicates that this model provides a considerably better fit to the experimental data than does the simpler one represented by the dashed line. Indeed, the fit would evidently be further improved by choice of an even larger value for the O–H$^+$ force constant.

Conclusions

These calculations strongly support the view that neglect of deviations from the rule of the mean and of transfer contributions associated with protonation by H_3O^+ do not seriously impair simple treatments of solvent isotope effects. The largest discrepancies, of the order of 10%, arise in the measurement of fractionation factors for species with a single exchangeable hydrogen, or in the treatment of relatively product-like proton transfer transition states.

The calculated secondary isotope effects for the nonreacting bonds of H_3O^+ decrease continuously as the transition state passes from reactant-like to product-like, while the primary isotope effect passes through a maximum. Careful application of existing experimental methods should allow use of the secondary isotope effects as a criterion of transition state structure and provide an adequate test of the predicted correlation between primary and secondary effects.

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Solvent Effects on Strong Charge-Transfer Complexes. IV. Trimethylamine and Sulfur Dioxide in the Vapor Phase

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Abstract: Thermodynamic constants for the formation of the 1:1 molecular complex between trimethylamine (TMA) and SO_2 have been obtained from PVT and vapor-density data for equimolar mixtures of these gases in the temperature range 35–44°. Results are in excellent agreement with those obtained previously from measurements of ultraviolet spectra. The present research supports the previous conclusion that the extinction coefficient and oscillator strength of the charge-transfer (CT) band of TMA–SO_2 are nearly the same in the gas phase as in the solvent heptane; in this respect the complex differs from all other CT complexes for which both gas-phase and solution data are available.

In previous publications we have reported thermodynamic and spectral data for the charge-transfer (CT) complex between trimethylamine (TMA) and sulfur dioxide (SO_2) in the vapor phase,[1] in the nonpolar solvent heptane,[1] and in the moderately polar solvents dichloromethane and chloroform.[2] An interesting result of these studies was that the intensity of the CT absorption band changes very little when the medium is changed from vapor to a solvent. This observation is at variance with results obtained from vapor-phase studies of CT complexes with iodine,[3–5] tetracyanoethylene,[5] and carbonyl cyanide[6] as acceptors. In these cases, much lower intensities for the CT band have invariably been found in the vapor phase as compared to solution, both for weak[3] and, with iodine, also for stronger adducts.[4,5] There seems reason, however, to question the reliability of previously reported extinction coefficients of vapor-phase CT complexes.

Unfortunately, only two vapor-phase complexes have been studied independently by different workers.[3–5,7] For the weak benzene–I_2 complex, one report[7] concluded that only the product of the formation constant (K_c) and the extinction coefficient for the CT band (ϵ) could be calculated. In the other case, that of the moderately strong diethyl sulfide–I_2 complex,[4,5] the reported values of ϵ differed by a factor of more than 3, although the ϵK_c product agreed to within experimental error. This is somewhat surprising, since in this case a sufficient amount of the acceptor was apparently in the complexed form at the highest donor concentrations to permit calculation of K and ϵ separately.[8,9] However, random and systematic errors in absorbances are considerably larger for vapor-phase studies than in solution. Moreover, limitations are imposed by the low volatility and instability of reactants and complexes. We feel, therefore, that published extinction coefficients and formation constants for vapor-phase CT complexes should be regarded as highly uncertain. Since it is possible to determine the product ϵK_c for a given complex with reasonable accuracy from vapor-phase spectral data, this situation seems to call for the determination of K_c by nonspectral methods (*e.g.*, from PVT or vapor-density data) whenever it is feasible. With these methods, only one parameter (K_c) has to be inferred from a set of measurements at varying concentrations of the reactants.[10] Consequently, an accurate value of K_c can be deduced for systems in which only a small percentage of either component is complexed, and spectral results for the ϵK_c product then will yield a reliable value for ϵ. To avoid lengthy extrapolations, the classical methods should preferably be employed in the same temperature range as for the spectral study. We have therefore initiated programs in our laboratories aimed at the determination of formation constants for CT complexes in the vapor phase by classical methods. Since the TMA–SO_2 complex is apparently an exception with regard to the relationship between vapor-phase and solution CT absorption intensities, we have studied this complex by two independent nonspectral methods, in the temperature range 35–44°. PVT data found in the literature[11] have been used to calculate K_c at higher temperatures.

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[1] J. Grundnes and S. D. Christian, *J. Amer. Chem. Soc.*, **90**, 2239 (1968).

[2] J. Grundnes and S. D. Christian, *Acta Chem. Scand.*, **23**, 3583 (1969).

[3] F. T. Lang and R. L. Strong, *J. Amer. Chem. Soc.*, **87**, 2345 (1965).

[4] M. Tamres and Y. M. Goodenow, *J. Phys. Chem.*, **71**, 1982 (1967).

[5] M. Kroll, *J. Amer. Chem. Soc.*, **90**, 1097 (1968).

[6] J. Prochorow, *J. Chem. Phys.*, **43**, 3394 (1965); J. Prochorow and A. Tramer, *ibid.*, **44**, 4545 (1966).

[7] W. K. Duerksen and M. Tamres, *J. Amer. Chem. Soc.*, **90**, 1379 (1968).

[8] W. B. Person, *ibid.*, **87**, 167 (1965).

[9] D. A. Deranleau, *ibid.*, **91**, 4044 (1969).

[10] S. D. Christian, E. E. Tucker, and H. E. Affsprung, *Spectrochim. Acta, Part A*, **23**, 1185 (1967).

[11] A. B. Burg, *J. Amer. Chem. Soc.*, **65**, 1629 (1943).