

tronegativity scale proposed here may merit general adoption because of the simple relationship with

and neglecting polarizabilities. It should be noted that this definition predicts a greater ionic character for a given electronegativity difference as the sum of the electronegativities decreases.

charge, inductive transmission of charge and dipole moment.

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Isotope Effects in Deuterium Oxide Solution. I. Acid-Base Equilibria

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It is suggested that the deuterium oxide solvent isotope effect on aqueous acid dissociation constants arises principally from changes in zero-point energy associated in turn principally with changes in hydrogen bonding strength and number on dissociation. These considerations lead to a simple quantitative method of estimating the isotope effect on acid-base equilibrium constants; this shows good agreement with experiment.

Solvent deuterium isotope effects are an important tool for the determination of the mechanism of reactions, particularly those catalyzed by acids and bases; *e. g.*, the observation that some acid catalyzed reactions are faster in deuterium than in protium oxide often is used as evidence that the conjugate acid of the reactant is an intermediate formed in an equilibrium step.

Understanding of these kinetic isotope effects can only follow our understanding of isotope effects upon reaction equilibria. This latter topic is the subject of this paper, which will be followed by another dealing with the more complex problems set by solvent kinetic isotope effects. We discuss equilibria first because the knowledge of initial and final state structure makes possible experimental justification of our treatment. In discussions of mechanism the structure of the transition state represents an additional unknown which leads to additional uncertainties and controversy.

The general theoretical considerations involved in the treatment permit qualitative predictions about isotope effects on acid-base equilibria. In addition, by choice of certain simple rules and the acceptance of assignment of certain vibrational frequencies a simple model is set up which provides generally satisfactory quantitative explanations of such effects.

It has long been known that protium oxide has a larger self dissociation constant than deuterium oxide^{2,3} and that dissociation constants of weak acids are larger in water than in deuterium oxide, the isotope effect being larger the weaker the acid.^{4,5} It has been suggested that these differences are related to the smaller zero point energy of the dissociated proton relative to a covalently bonded hydrogen.^{2,3,6}

This difference of dissociation constants gives a ready explanation for the greater rate in deuterium oxide (by factors up to 3) of those acid catalyzed

reactions in which the rate depends on an equilibrium concentration of the conjugate acid of the reactants.⁶

By making certain reasonable approximations one can express the deuterium isotope effect upon a reaction equilibrium constant, between the initial state having a sum of the vibration frequencies for the isotopically substituted hydrogen atoms, $\Sigma\nu_H$, and a final state having a corresponding sum $\Sigma\nu_{H'}$, by the expression⁷

$$\Sigma\nu_H - \Sigma\nu_{H'} = 12.53 T \log K_H/K_D$$

The dissociated proton exists in water solution as the hydronium ion, H_3O^+ ,⁸ which is strongly hydrogen bonded to three adjacent water molecules. Recently the vibration frequencies of this ion in solution have been assigned.⁹ The stretching vibration frequencies of the hydronium ion in concentrated solution lead to a broad band centered at 2900 cm^{-1} , appreciably lower than the corresponding absorption of water, 3400 cm^{-1} . This difference, however, of itself is not sufficient to explain the deuterium isotope effect upon the autoprotolysis of water, $K_{H_2O}/K_{D_2O} = 6.5$.¹⁰ Further it gives no explanation of the dependence of relative acid dissociation constants in water and deuterium oxide upon the strength of the acid.

The clue which leads to a general explanation of these observations is the fact that the ratio K_{H_2O}/K_{D_2O} for the dissociation of acids decreases as the acid becomes stronger. Since all acids partially dissociate in water to the hydronium ion and a con-

(7) This equation, an approximation of a more exact and general formulation of the effect of isotopic substitution on reaction rate published by Bigeleisen (see ref. 13), involves the assumption that all of the isotope effect is due to zero-point energy differences and that the reduced mass relationship holds between the vibration frequencies of hydrogen and deuterium. For further discussion of these approximations see A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *THIS JOURNAL*, **80**, 2326 (1958). Explicitly neglected are any isotopic entropy effects, tunnelling and anharmonicity. Within the accuracy of the present calculations these limitations should not be serious.

(8) (a) M. Eigen, L. deMaeyer and W. J. Hamer, "The Structure of Electrolytic Solutions," John Wiley and Sons, New York, N. Y., 1959, chap. 5; (b) B. E. Conway, J. O'M. Bockris and H. Linton, *J. Chem. Phys.*, **24**, 834 (1956).

(9) M. Falk and P. A. Giguère, *Can. J. Chem.*, **35**, 1195 (1957).

(10) R. W. Kingerly and V. K. LaMer, *THIS JOURNAL*, **63**, 3256 (1941).

(1) National Science Foundation Senior Postdoctoral Fellow and Alfred P. Sloan Research Fellow.

(2) G. N. Lewis and P. W. Schutz, *THIS JOURNAL*, **56**, 1913 (1934).

(3) O. Halpern, *J. Chem. Phys.*, **3**, 456 (1935).

(4) C. K. Rule and V. K. LaMer, *THIS JOURNAL*, **60**, 1974 (1938).

(5) D. C. Martin and J. A. V. Butler, *J. Chem. Soc.*, 1366 (1939).

(6) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

jugate base we must consider the effects of replacement of hydrogen by deuterium upon the vibration frequencies of both these species, relative to the initial state. With regard to the undissociated acid molecules it is known that the free O-H vibration frequencies of a series of oxy-acids are dependent upon the strength of the acid,¹¹ but these variations are too small to account for the observed influence on isotope effects. However in aqueous solution we must consider not the O-H frequencies of the free acid, but those which pertain to that acid when it is hydrogen bonded to solvent water molecules. The strength of these hydrogen bonds will depend upon the strength of the acid. In the systems which have been studied the frequency shift produced by the hydrogen bonding of a given donor varies linearly with the pK_b of the acceptor.¹² Although there are no comparable data relating to different acidic donors, it is reasonable to assume that the frequency shift produced by hydrogen bonding to a given acceptor will be directly proportional to the pK_a of the donor. This gives a method for the estimation of the stretching frequency of acidic hydrogens in water and hence a partial explanation for the dependence of the ratio K_{H_2O}/K_{D_2O} upon the strength of the acid concerned.

Also to be taken into account is the fact that the conjugate base, formed by dissociation of the weak acid, will itself be hydrogen bonded to water molecules, and it is expected that here the frequency shift produced by hydrogen bonding will vary linearly with the pK_b of the base acting as acceptor to the hydrogen atoms of water.

The final point to be considered is a statistical one. The hydronium ion in solution has three protons, which can be donated to form strong hydrogen bonds,⁸ and the hydroxide ion, or other oxide ions, RO^- , can accept three strong hydrogen bonds from the solution. Thus in considering the frequency shifts produced by a chemical change not only the strengths of the hydrogen bonds which are made and broken must be considered but also the number of such hydrogen bonds; all the primary hydrogen bonding changes must be accounted for.

To do this in a simple and consistent way we have adopted the rules listed below. Some of these are of necessity somewhat arbitrary and their application to certain systems can be criticized in detail. We apply them without discrimination to avoid bias in individual cases. These rules are:

a. Each water molecule in the absence of solute is assumed to accept two hydrogens from, and to donate two hydrogens to, other water molecules for hydrogen bonding.

b. All solute molecules are assumed to hydrogen bond by interaction with solvent-water molecules only. This excludes hydrogen bonding interaction between solute molecules, and this model will not apply unchanged to molecules or ions with strong intramolecular hydrogen bonds.

c. Solute molecules more basic than water will accept hydrogens from water for hydrogen bond-

ing, for as many basic sites (*i.e.*, as many electron lone pairs) as are available. For bases having more than one stable resonance contributing form, only the electron pairs which in a molecular orbital representation are not delocalized are assumed to act as acceptor sites. In acid solutions which contain an excess of hydrogen bonding donors, bases weaker than water may accept hydrogen bonds.

d. Solute molecules more acidic than water will donate their hydrogens for hydrogen-bonding to water, by breaking one or more of the hydrogen bonds already existing in water. Thus for every hydrogen bond donated by an added acid the acid molecule must accept another itself or one will be left unaccepted in the surrounding solution.

e. The number of hydrogen bonds donated and accepted must be the same on each side of the chemical equation, *i.e.*, the hydrogen bonding "equation" must be balanced in the way that the proportions in any chemical equation are balanced.

Dissociation Constant of Water.—This discussion of the importance of hydrogen bonding allows qualitative predictions to be made about the direction and magnitude of solvent deuterium isotope effects upon equilibria. By combining these rules with the known vibrational frequencies of water, the hydronium ion and the hydroxide ion we can estimate the isotope effect on the autoprotolysis of water, although such a calculation must suffer from the uncertainties in the assignments of the frequencies concerned. These uncertainties are particularly acute for the very broad bands observed in aqueous systems. The two stretching vibrations, ν_1 and ν_3 , for liquid water are each near to 3400 cm.^{-1} , while the bending vibration, ν_2 , is at 1640 cm.^{-1} and the absorption at 710 cm.^{-1} has been assigned to a libration.^{9,14,15}

This latter frequency is due essentially to the same mode as that observed at 670 cm.^{-1} for various alcohols in the associated state¹⁶ and described as an out of plane deformation vibration of the RO-H bond. In water it must include three approximately degenerate vibrations of this type.

There is some uncertainty in the exact values for the liquid water vibration frequencies largely because the bands are broad and ill-defined. The two stretching frequencies are not exactly the same but their separate observation is difficult because coupling between the two O-H oscillators broadens the bands. Van Eck and co-workers¹⁵ overcame this difficulty by observation of the OH and OD stretching frequencies of HOD, assigning an approximate value of 3400 cm.^{-1} to the former. This figure corresponds with the peak of the broad absorption maximum observed in liquid H_2O itself. A similar difficulty arises in the assignment of the two stretching frequencies of the hydronium ion; analogy suggests that here also no great error is involved in using the value of the absorption maximum as the average of the two OH stretching frequencies.⁹ All of the frequencies given including the libration ones are essentially hydrogen

(14) P. A. Giguère and K. B. Harvey, *Can. J. Chem.*, **34**, 798 (1956).

(15) C. L. P. van Eck, H. Mendel and J. Fahrenfort, *Proc. Roy. Soc. (London)*, **247A**, 472 (1958).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 163.

(12) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941).

(16) A. V. Stuart and G. B. Sutherland, *J. Chem. Phys.*, **24**, 559 (1956).

vibrations and shift by about the theoretical factor when the hydrogens are replaced by deuterium indicating that anharmonicity effects in these vibrations are small. Since the vibration frequencies for water vapor are known accurately, as is the differential heat of vaporization of H_2O and D_2O , calculation of this latter value from the vibration frequencies of the two states serves as a check on the frequency assignments in the liquid. Using 3651, 3755 and 1595 cm^{-1} for the vibration frequencies of water vapor¹⁷ and those given above for liquid water the equation of Bigeleisen¹⁸ gives a $\Delta\Delta H$ vap. of 486 cal./mole at 0°. The observed value is 407.¹⁹ The calculated value assumes complete hydrogen bonding in the liquid state. If the frequencies are accurate and the assignments correct this might be taken to indicate a hydrogen bonding proportion of 407/486 or 84% at 0°. This is close to values (75% to 100%) previously estimated for this quantity. The calculated values for $\Delta\Delta H$ at higher temperatures are relatively larger than the observed ones, probably indicating a relatively smaller proportion of hydrogen bonding at higher temperatures, as already suggested by other workers; e. g., the proportion comes out about 55% at 100°.

For aqueous H_3O^+ the symmetrical stretching frequency, ν_1 , is 2900 cm^{-1} as is the doubly degenerate asymmetrical stretching frequency, ν_3 . The symmetrical bending frequency, ν_2 , is 1205 cm^{-1} while the doubly degenerate asymmetrical bending frequency, ν_4 is 1750 cm^{-1} .⁹ The three libration frequencies of the hydronium ion in solution have not been assigned, but the 710 cm^{-1} band observed in water is shifted toward 600 cm^{-1} by concentrated strong acid,⁹ and as no bands higher in frequency which could be associated with these modes were detected, they can tentatively be assigned this value. A possible source of error in our treatment is the use of these frequencies observed of necessity in concentrated acid solution for calculations relating to dilute acid. The frequencies for the hydroxide ion in solution are not all known, but these should be closely approximated by the known values for the solid lithium hydroxide hydrate.²⁰ The O-H stretching frequency is 3574 cm^{-1} and the hydrogens of water donated for hydrogen bonding to hydroxide absorb at approximately 3000 cm^{-1} .²⁰ The value for the O-H stretching frequency of the hydroxide ion, in water, is known to be very near 3600 cm^{-1} from Raman spectra.²¹ Similar data indicate that the O-H stretching frequency of unassociated water in the liquid is also 3600 cm^{-1} . The frequency of O-H vibrations of non-hydrogen bonded alcohols is 3650 cm^{-1} in carbon tetrachloride. The slightly lower frequency in water arises presumably from its higher dielectric constant.²² For the purpose of convenience of calculation the non-hydrogen bonded OH stretching frequencies of hydroxide ion,

(17) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, New York, N. Y., 1945, p. 281.

(18) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(19) I. Kirshenbaum, "Physical Properties and Analysis of Heavy Water," McGraw-Hill Book Co., New York, N. Y., 1951, p. 30.

(20) L. H. Jones, *J. Chem. Phys.*, **22**, 217 (1954).

(21) J. H. Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939, Ch. 22.

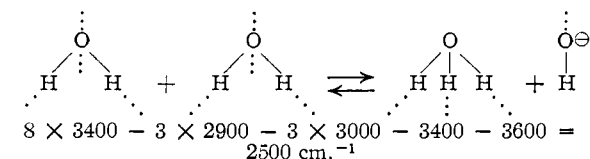
(22) M. L. Josien and N. Fuson, *J. Chem. Phys.*, **22**, 1169 (1954).

water and alcohols is taken as 3600 cm^{-1} . No observations of the two hydroxide ion libration frequencies have been reported.

The frequencies involved in the autoprotolytic dissociation equilibrium are therefore

	$2H_2O \rightleftharpoons H_3O^+ + ^-OH$		
Number of stretching vibrations	4	3	1
Number of bending vibrations	2	3	0
Number of libration modes	6	3	2

The number of stretching frequencies is always equal to the number of hydrogen atoms while the number of bending plus librational modes always equals twice the number of hydrogen atoms. These latter two types can be considered to be the two vibrational components of the hydrogen in directions perpendicular to the O-H bond. The total change in stretching frequencies, including all of the hydrogen bonds donated to and accepted from other solvent molecules, as indicated by the dotted lines shown in the equation, is



The 3400 figure is subtracted because the hydrogen of the hydrogen bond which was accepted by one of the water molecules in the initial state must be accepted by another solvent water molecule in the final state (rule e, above).²³ A site in the solution is available for this as the hydrogen atom of the hydroxide ion is not donated for hydrogen bonding; it is considered to be too weakly acidic to be an effective donor, just as the oxygen of the hydronium ion is considered to be too weakly basic to be an effective acceptor. Thus the number of hydrogens donated and accepted is kept constant through the chemical change indicated by the equation. The accounting of the frequency changes in the bending and librational modes is difficult because of the uncertainties in, and lack of, assignments noted above. If the two $\bar{O}H$ librations are assigned the same value, 600 cm^{-1} , as that suggested above for the hydronium ion then the net change in these modes is

$$2 \times 1640 + 6 \times 710 - 2 \times 1750 - 1205 - 5 \times 600 = -165 \text{ cm.}^{-1}$$

Thus the contributions from these frequencies essentially cancel one another. This is in accord with the general observation that hydrogen bending frequencies are not very sensitive to hydrogen bond strength;²⁴ e.g. the bending frequency in ice is 1640 cm^{-1} and in water 1595 cm^{-1} . Ignoring this contribution and assuming that all the frequency changes are in the stretching modes, the calculated value for the isotope effect, K_{H_2O}/K_{D_2O} , is

$$\text{antilog } 2500/3760 = 4.6 \text{ (at } 300^\circ K.)$$

This is in fair agreement with the reported value of 6.5,¹⁰ all but 550 cm^{-1} or 18% of the expected frequency change having been accounted for.

(23) It is assumed that the lyate and lyonium ions hydrogen bond only with water molecules and not with each other, see rule b, above.

(24) E. Greinacher, W. Luttker and R. Mecke, *Z. Elektrochem.*, **59**, 23 (1955).

Dissociation of Other Weak Acids.—The same approach used for water should also allow the calculation of the solvent deuterium isotope effect on the dissociation of other weak acids, but the difficulty is that the frequencies of the hydrogen bonds between the solvent and these acids and their conjugate bases are not known. However, as already mentioned, the work of Gordy and Stanford¹¹ gives a method for the estimation of these frequencies because these authors found that the O-H stretching frequencies of hydrogen bonds donated to various acceptor molecules were linearly dependent on the basicity of the acceptor molecules. These results referred to solutions in relatively non-polar, non-hydroxylic solvents and therefore the frequencies of hydrogen bonds donated from water to similar acceptor molecules in aqueous solution would be expected to lie on a line lower in frequency than that of Gordy and Stanford; Josien and Fuson have shown that hydrogen bond strength increases with increasing dielectric constant of the solvent.²² The frequency of the hydrogens donated from water to the hydroxide ion (acting as an acceptor), $pK_b = -1.74$, is $\nu = 3000 \text{ cm.}^{-1}$, and for that donated from water to water as a base, $pK_b = 15.74$, is $\nu = 3400 \text{ cm.}^{-1}$. These values can be used to define a line applicable to hydrogen bonds donated to oxygen bases in water solutions

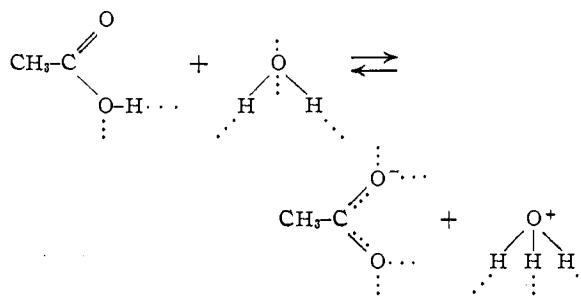
$$\nu (\text{cm.}^{-1}) = 3040 + 22.9 pK_b \quad (\text{a})$$

Similarly, if one assumes that the strength of hydrogen bonds accepted by water from acids will be proportional to the strength of the acid, the values of hydronium ion donating to water, pK_a (per proton) = -1.26 , $\nu = 2900 \text{ cm.}^{-1}$, and water donating to water, pK_a (per proton) = 16.04 , $\nu = 3400 \text{ cm.}^{-1}$, can be used to define a correlation line for oxygen acids

$$\nu (\text{cm.}^{-1}) = 2937 + 28.8 pK_a \quad (\text{b})$$

In applying these equations the pK_a values are corrected statistically for the number of acidic protons. These lines cannot continue linearly when extended into extreme values of pK_a or pK_b , but in subsequent calculations we assume that they do so at the low frequency end of the scale far enough to include all strong acids and strong bases involved. Thus the lowest stretching frequencies used in any of the subsequent calculations are around 2500 cm.^{-1} , and this does not closely approach those for very strong hydrogen bonds such as 1450 cm.^{-1} HF_2^- .²⁵ The straight lines are used to estimate frequencies of weak hydrogen bonds up to the limit of 3600 cm.^{-1} which is the frequency used for all free O-H stretching modes in water solution. Any values calculated from equation a which come out greater than this are replaced by this value.

As an example, we outline the calculation of the deuterium oxide solvent isotope effect upon the dissociation constant of acetic acid. In the equation the "dangling" dotted lines represent hydrogen bonds to or from solvent water molecules. According to rule c, acetate ion would accept four hydrogen bonds and by rule d acetic acid donates one and accepts one.



$$\begin{aligned} pK_a (\text{acetic acid}) &= 4.74 \\ pK_b (\text{acetate ion}) &= 9.26; pK_b (\text{per oxygen atom}) = 9.56 \\ pK_b (\text{acetic acid}) &= 20.2^{25} \end{aligned}$$

The stretching frequencies of the hydrogen bonds involved are therefore estimated as

$$\begin{aligned} \text{Accepted by acetic acid, } \nu &= 3503 \text{ cm.}^{-1} \\ \text{Donated by acetic acid, } \nu &= 3074 \text{ cm.}^{-1} \\ \text{Accepted by acetate ion, } \nu &= 3259 \text{ cm.}^{-1} \end{aligned}$$

For the initial state: $\Sigma \nu_H = 5 \times 3400 + 3074 + 3503 = 23,577 \text{ cm.}^{-1}$.

For the final state: $\Sigma \nu_H = 4 \times 3259 + 3 \times 2900 = 21,736 \text{ cm.}^{-1}$. The fifth frequency at 3400 cm.^{-1} in the initial state is for a solvent-solvent bond which must be broken to generate the fourth bond to be accepted by the acetate ion (rule e). The calculated isotope effect using the equation given above is

$$K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = \text{antilog} \frac{\Sigma \nu_H - \Sigma \nu_H'}{3760} = 3.1 \text{ at } 300^\circ \text{K.}$$

This compares well with the observed value of 3.33, and it seems that neglect of the bending modes has introduced no serious error. The table compares the observed isotope effects on the dissociation constants of some weak acids with those calculated by the method outlined above. The agreement is seen to be good; possibly this is in part due to the compensation of errors in the assumptions used to obtain the frequencies. However, it would seem that the main assumptions and the basic outline of the calculations are correct even if the frequencies required are obtained by crude approximations. It should be stressed that no adjustable parameters were used, and no frequencies were selected to give the correct trend in the results; the values of $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}}$ are not particularly sensitive to the actual frequencies chosen, e.g., an uncertainty of 100 cm.^{-1} would change the ratio by 6%.

Dissociation of Strong Acids.—Apparently the deuterium isotope effect on the dissociation constant has only been estimated for one or two strong oxygen acids.²⁷ However, practically all the conjugate acids involved in acid catalyzed mechanisms to which the solvent deuterium isotope effect criterion have been applied will be as strong or stronger than H_3O^+ and as mentioned above it is believed that the isotope effect on the dissociation constant is at least in part the cause of this kinetic deuterium isotope effect. The treatment of kinetic effects can only be done by comparing the transition and initial states, and so the effect upon pre-equilibrium constants is not expressly considered in our later discussion of kinetic isotope effects.

(26) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 40 (1957).

(25) G. L. Coté and H. W. Thompson, *Proc. Roy. Soc. (London)*, **210A**, 206 (1951-1952).

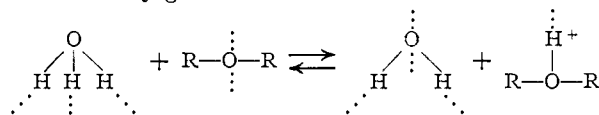
(27) J. G. Pritchard and F. A. Long, *This Journal*, **80**, 4162 (1958).

TABLE I
ISOTOPE EFFECT OF DEUTERIUM OXIDE SOLVENT ON THE
DISSOCIATION OF WEAK ACIDS

Acid	pK_a	K_{H_2O}/K_{D_2O} (obsd.)	K_{H_2O}/K_{D_2O} (calcd.)
Water	15.74	6.5 ^a	4.6
β -Trifluoroethanol	12.4	4.4 ^b	4.5
HCO_3^-	10.25	4.4 ^c	3.8
<i>p</i> -Nitrophenol	7.21	3.67 ^d	3.3
Acetic acid	4.74	3.33 ^d	3.1
Chloroacetic acid	2.76	2.76 ^d	2.8

^a Ref. 10. ^b P. Ballinger and F. A. Long, THIS JOURNAL, 81, 2347 (1959). The pK_b of the alcohol was assumed to be 18. ^c P. Glasoe and F. A. Long, J. Phys. Chem., 64, 188 (1960). ^d D. C. Martin and J. A. V. Butler, J. Chem. Soc., 1366 (1939).

At first sight it might seem that the dissociation of acids as strong as H_3O^+ would show no deuterium isotope effect. This is not so, because there is the statistical factor related to the number of protons possessing the characteristic acidity. Thus the hypothetical ether, R-O-R, having the same basicity as water will, in acid solution, be in equilibrium with its conjugate acid



This conjugate acid, on the assumptions outlined above, will have the same O-H stretching frequency as H_3O^+ , but in its production from H_3O^+ three strongly acidic protons have been replaced by only *one*. Thus while the transferred proton, in this hypothetical case, retains the same vibration frequency, the two protons left behind as H_2O each gain about 500 cm.^{-1} in frequency. This isotope effect on the equilibrium written above is then

$$K_{D_2O}/K_{H_2O} = \text{antilog} \frac{1000}{3760} = 1.85$$

The "statistical" factor is very important and is not readily overcome by changes in acid strength. The weakest bases so far used in application of the solvent deuterium isotope effect criterion have conjugate acid pK_a 's around -7 . If this were the pK_a of the hypothetical ether the calculated K_{D_2O}/K_{H_2O} ratio would be reduced only to about 1.5. The statistical factor obviously is less important in cases where the conjugate acid has two equivalent protons, as in ROH_2^+ . Conjugate acids of hypothetical alcohols similar to the ethers mentioned above and having pK_a 's of -1.74 and $+7.0$ would show K_{D_2O}/K_{H_2O} values of about 1.4 and 1.0, respectively.

The calculation of this value for any specific acid is of course dependent in part on the detailed structure of the acid and conjugate base and particularly on how the hydrogen bonding is affected by structure. Pritchard and Long²⁶ have interpreted the data of Schubert and Burkett²⁸ to indicate that the ratio of the dissociation constant of the conjugate acid of mesitaldehyde, $pK_a = -4.6$, in aqueous acid to that in the deuterated solvent is 2.3. Our estimated value using the method described above is 1.6 giving not exceptionally good

(28) W. M. Schubert and H. Burkett, THIS JOURNAL, 78, 64 (1956).

agreement. However, Bigeleisen and Högfeldt²⁹ recently have determined K_{H_2O}/K_{D_2O} to be 1.4 ± 0.1 for the conjugate acid of benzalacetophenone, $pK_a = -5.73$. For this compound the method described here gives an estimated value of K_{H_2O}/K_{D_2O} of 1.5 in excellent agreement with experiment. This is the only oxygen base for which these authors report the isotope effect on the dissociation constants, most of their rather extensive measurements having been done on nitrogen bases. The Högfeldt and Bigeleisen paper, which appeared after most of the work in the paper was finished, considers also some of the theoretical aspects of the deuterium solvent isotope effect on acidity constants. These authors point out that to a first approximation the isotope effect will depend on zero point energy changes in the ionization process. They observe that while there is expected no general correlation between acidity and isotope effect independent of acid type, within a series including acids of a given type there should be some small dependence on pK_a . This agrees with our treatment in that we have herein limited it to a consideration of oxygen acids and bases, but we believe that it could be extended successfully to include nitrogen bases provided that data on the relevant frequencies are available. Thus our treatment predicts no smooth correlation of isotopic effect on dissociation with pK_a independent of structure but shows how changes in pK_a and particularly changes in structure will both combine to influence the isotope effect. In addition we stress the importance of hydrogen bonding interactions of both acids and bases with solvent in determining the isotope effects and the dependence of hydrogen bond strength (and therefore zero point energies) on acidity and basicity.

In view of the several obvious limitations on the accuracy of these calculations imposed by the scarcity of the data and the simplicity of the model, it is indeed surprising that the method outlined gives results which, within the probable error of measurement, are identical with most of the experimental values. Even though this agreement is almost certainly in part the result of compensating errors, we think that it nevertheless indicates that the main points of the model are correct and that the isotope effects on the dissociation constants arise principally from primary hydrogen bonding interactions of the acids and bases with the solvent and further that the dependence of isotope effect on acid strength is the result of dependence of hydrogen bond vibration frequency on acidity and basicity. We have deliberately used frequency assignments already made by others even though in some cases there would be some justification for choosing a different frequency which would give better results in our calculations. Whenever possible we have chosen frequencies determined on aqueous solutions. No doubt future, more refined measurements will change some of these values. Probably the greatest uncertainty centers on the value of 3000 cm.^{-1} for the stretching frequency of the hydrogen bond donated by water to hydroxide ion. It is reasonable to believe this value is too

(29) E. Högfeldt and J. Bigeleisen, *ibid.*, 82, 15 (1960).

high, because the hydroxide is not fully hydrated in crystalline lithium hydroxide monohydrate. A further problem is that the experimental values for the autoprotolysis ratio, $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}}$, refer to dilute solutions, whereas the spectroscopic data for the hydronium ion in water refers to concentrated solutions of acid. Thus the hydronium ion in these solutions may not be fully hydrated; if this is so then the stretching frequency for H_3O^+ should be lower than 2900 cm.^{-1} , the value used in our calculations.

The comparatively poor agreement between the experimental and calculated values for the isotope effects on water autoprotolysis would be much improved by the choice of slightly lower values for the stretching frequencies of the hydroxide and hydronium ions. Such changes will have less effect upon the calculations for dissociations of acids other than water, because we relate their frequencies to those of water and its ions. Therefore the effect of anticipated future changes in the frequencies assigned to water and its ions will be partially self-cancelling in all of our calculations except for the autoprotolysis equilibrium.

Further improvement in this type of calculation will depend on the observation of more hydrogen bond stretching frequencies for different solvated acids and bases. This pertains particularly to the

extension of the method to acids and bases containing nitrogen and other electronegative atoms. However, even for acid-base equilibria in which the relevant frequencies are not known, or cannot be estimated, it is possible to predict the direction of changes in the ratio $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}}$ with changes in the dissociation constants and the effect of changing the number of equivalent ionizable, hydrogen atoms in the acid. One major limitation which will be difficult to surmount is the neglect of the bending frequency changes. This seems to impose some absolute limit on the possible refinement of the method as the detailed accounting of these frequencies for any large number of examples would be extremely difficult, although we have shown this neglect not to be serious in the calculations relating to the autoprotolysis of water.

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Effects on Polarographic Waves of the Formation of Insoluble Films on Dropping Mercury¹

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The formation of films of insoluble substances on the surface of dropping mercury may exert two different effects on polarograms: suppression of maxima and alteration of the characteristics of polarographic waves. Considerably less than a monomolecular film of mercurous iodide completely suppresses maxima of both the first and the second kind. Experimental results presented in this paper show that the mercurous iodide film behaves like an anionic surface-active organic compound in regard to its effect on the characteristics of polarographic waves. The film makes the reduction wave of aquo-copper(II) ions more reversible, while that of oxygen is made more irreversible. The reduction of persulfate is strongly inhibited in the potential range where the mercurous iodide film is formed.

It is well known that the addition of small amounts of surface-active organic compounds suppresses polarographic maxima, while those substances often change the shape of polarograms. Similar effects are observed when a film of insoluble substances is formed on the dropping mercury.

Lingane² reported that the maximum on the reduction wave of lead ions in $0.1 M$ potassium chloride is completely suppressed when the solution is made $0.001 M$ with respect to iodide ions but gave no interpretation. We found that even at a much smaller concentration of iodide, e.g., $10^{-5} M$, complete suppression of maxima is observed, not only of lead but also of oxygen, copper(II), mercury(II), iron(III) and persulfate, while in the same supporting electrolytes pronounced

maxima were observed in the absence of the trace of iodide. Iodide is effective in suppressing maxima only in the potential range where mercurous iodide is formed anodically. From this experimental fact as well as from characteristics of electrocapillary curves and anodic iodide waves at both the conventional and the rotating dropping mercury electrode, it is concluded that the maximum suppression effect of iodide is due to the formation of a film of mercurous iodide. Bromide and chloride ions also form a film of their mercurous salts and suppress maxima in the potential range where these films are formed. Small amounts of a phenylmercuric salt are also effective in suppressing maxima in the potential range where this substance is reduced to form insoluble diphenylmercury.^{3,4} Effects of the films on the characteristics of the reduction waves of persulfate,

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