and 290∼300°, respectively. The value of $\bar{n}$ of the distillation residue was about 10.

Owens, *et al.*, reported that extensive decomposition was found in the pot in distilling the reaction product formed at 0∼4° in an equimolar mixture of isopropyl acrylate and phenylmagnesium bromide in ether.[12] Under the conditions we adopted for preparation of samples and distillation, chemical change in distillation was not found in the distillate except the H–D exchange described previously and formation of isopropyl alcohol described below. In the distillation at bath temperatures above 250°, isopropyl alcohol was found in the distillate trapped at −80° but was absent in the distillate trapped at room temperature. No other decomposition products were found in the spectrum of the distillate. The amount of isopropyl alcohol found in the distillate was about 3% of the amount of isopropyl groups found in the oligomer mixture before the distillation.

Phenylmagnesium bromide was prepared in ether without using any initiator. The Br/Mg ratio was found to be 1.00 ± 0.01 by Mohr's method for bromine and acid titration for basic magnesium. The phenyl/magnesium ratio was found to be 0.95 by measuring the amount of iodobenzene formed by adding an ether solution of iodine on a vapor phase chromatograph.[13] Magnesium dibromide was prepared from dibromoethylene and magnesium metal in ether. α,β-d_2 monomer with $\gamma = 6$ was prepared by adding heavy hydrogen to isopropyl propiolate using the Lindlar catalyst[14,15] as described previously.[8] α,*cis*-β-d_2 monomer was prepared by reducing isopropyl propiolate in heavy water by a method analogous to that of Botti and Furman.[16] The γ value of the monomer was adjusted to $^1/_6$ by adding a small amount of the monomer with $\gamma = 6$. β-d_1 monomer with $\gamma = {}^1/_6$ was obtained by hydrogenation of isopropyl propiolate-β-d_1 using the Lindlar catalyst.[14,15] The deuterated propiolate (99% D) was prepared from isopropyl propiolate by repetitions of H–D exchange with heavy water added with a trace of sodium metal (refluxed for 3 hr in each time), followed by neutralization with a deuterated aqueous solution of sulfuric acid.

Nmr spectra were measured by a Varian HR-100 spectrometer.

Acknowledgment. The authors gratefully acknowledge the suggestions of Professor Conrad Schuerch, State University College of Forestry at Syracuse, regarding English usage.

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Isotope Effects on the Basicity of 2-Nitrophenoxide, 2,4-Dinitrophenoxide, Hydroxide, and Imidazole in Protium Oxide–Deuterium Oxide Mixtures[1,2]

Lipot Pentz and Edward R. Thornton

Contribution from the Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19104. Received May 22, 1967

Abstract: The ion product of D_2O was found to be $1.38 \times 10^{-15}\ M^2$ at 25° using precisely calibrated glass electrode measurements. The ion products of D_2O–H_2O mixtures have also been precisely measured. The value of the constant $K_n{}'$ for the equilibrium $DO^- + ({}^1/_2)H_2O \rightleftharpoons HO^- + ({}^1/_2)D_2O$ was calculated by nonlinear least squares to be 2.120 ± 0.190 at 25° from our data on the dissociation of 2-nitrophenol; data on other acids from the literature, used in similar calculations, gave similar values for $K_n{}'$. Precise data on imidazole in D_2O–H_2O mixtures has also been determined. Corrections for measurements of pL (L = H and/or D) in D_2O–H_2O mixtures (using a glass electrode and pH meter) are given.

Constant K for equilibrium 1 is determined by the autoprotolysis constants of pure isotopic light and

$$2H_2O + D_3O^+ + DO^- \overset{K}{\rightleftharpoons} 2D_2O + H_3O^+ + HO^- \qquad (1)$$

heavy water: $K = K_{H_2O}/K_{D_2O}$; or by the constants of the exchange equilibria (2 and 3)

$$2D_3O^+ + 3H_2O \overset{L}{\rightleftharpoons} 2H_3O^+ + 3D_2O \qquad (2)$$

$$2DO^- + H_2O \overset{(K_n')^2}{\rightleftharpoons} 2HO^- + D_2O \qquad (3)$$

since $K = L^{0.5}K_n{}'$.

K_{D_2O} has been determined by several authors[3-8] and K calculated; the values range from 5.17[4] to 7.4.[8]

L can be deduced from the exchange constant of the reaction

$$2D_3O^+ + 3H_2O + 2Cl^-(D_2O) \overset{L'}{\rightleftharpoons} 2H_3O^+ + 3D_2O + 2Cl^-(H_2O) \qquad (4)$$

taking into account the different activities of chloride ion in H_2O and in D_2O

$$L' = L\frac{(\gamma_{Cl^-})^2{}_{H_2O}}{(\gamma_{Cl^-})^2{}_{D_2O}}$$

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where the activity coefficients γ are both defined relative to the same standard state; *e.g.*, the gaseous chloride ion at 1 atm and 25°.

Purlee[9] calculated L as 11.0 from emf measurements and showed that the Gross equation[10] predicted acid dissociation constants and reaction rates in D_2O–H_2O mixtures well when this value of 11.0 was used. Swain and Bader[11] employed Raman and infrared spectroscopic data to calculate $\Delta G°$ for exchange process 4 and to obtain the difference in the free energy of solvation of Cl^- in the two waters. The resulting value of L is 8.20.

$L^{-1/6} = l$ can be determined directly by nmr measurements of aqueous acid solutions. Assuming three equivalent hydrogens in the hydrated lyon (lyonium ion), Kresge and Allred[12] reported l = 0.68; Gold,[13] l = 0.68 and 0.69. Heinzinger and Weston reported l = 0.70[14] using a liquid–vapor fractionation technique.

The relative basicity of DO^- and HO^- has not been extensively studied. K_n' has been usually obtained from certain accepted values of K and L. Swain and Bader[11] calculated a value of 1.79. Ballinger and Long[15] found that the relative rates of the base-catalyzed epoxide formation from 2-chloroethanol and 2-chloropropanol followed the equation derived for specific hydroxide catalysis by Nelson and Butler,[10] when the value of 1.97 was employed for K_n'. Kresge and Allred[12] suggested a tentative K_n' = 1.25 based on nmr measurements on strongly basic solutions of D_2O and H_2O. Heinzinger and Weston measured, by vapor–liquid fractionation, a value of K_n' = 2.10 at 13.5°.[16]

The investigation of base-catalyzed reactions in our laboratory[17] led us to study the dissociation of weak acids in D_2O–H_2O solvents in order to estimate the value of K_n'.

Discussion and Results

Upon the basic association of the conjugate bases of weak acids in isotopic waters, the equilibria given by (5) are established.

$$\begin{aligned} A^- + H_2O &\overset{K_{B,H}}{\rightleftharpoons} AH + HO^- \\ A^- + D_2O &\overset{K_{B,D}}{\rightleftharpoons} AD + DO^- \end{aligned} \qquad (5)$$

The isotope effect in equilibria 5 combines an equilibrium primary isotope effect for the transfer of L (H or D), a secondary isotope effect for the different basicities of HO^- and DO^-, and possibly a medium effect if the relative solvation of the acid and its conjugate base is dependent on the solvent composition. In mixed solvents there will be two more equilibria established, similar to those of eq 5. Equilibria 6

$$\begin{aligned} A^- + HDO &\rightleftharpoons AH + DO^- \\ A^- + HDO &\rightleftharpoons AD + HO^- \end{aligned} \qquad (6)$$

are similar to those described by the Gross equation, with the difference that here the lyon (proton or deuteron) donor is a neutral solvent molecule L_2O instead of L_3O^+.

For reactions involving the S^+H---O^-H type of transition states of reactant S, an equation for the isotope effect has been derived.[18] A derivation, similar in principle, can be made for equilibria involving negatively charged reactants.

The equilibrium constant, $K_{B.\alpha}$, in a mixed solvent of composition α (α is the *atom* fraction of deuterium in the solvent, (D)/[(D) + (H)]), can be expressed as

$$K_{B,\alpha} = \frac{\{[AH] + [AD]\}\{[HO^-] + [DO^-]\}}{[A^-]\{[H_2O] + [HDO] + [D_2O]\}}$$

and the equilibrium constant ratio, $K_{B,\alpha}/K_{B.H}$, as

$$\frac{K_{B,\alpha}}{K_{B,H}} = \frac{\{[AH][HO^-] + [AH][DO^-] + [AD][HO^-] + [AD][DO^-]\}[A^-][H_2O]}{\{[A^-][H_2O] + [A^-][HDO] + [A^-][D_2O]\}[AH][HO^-]} \qquad (7)$$

where all concentrations are equilibrium concentrations in the mixed solvent of atom fraction α. However, $K_{B,H}$ is experimentally measured in pure H_2O; eq 7 is valid for experimental $K_{B,\alpha}$ and $K_{B,H}$ only if there are no medium effects. The absence of medium effects can be assumed: because the uncharged water species H_2O, D_2O, and HDO form ideal solutions,[19] because DO^- and HO^- leave the hydrogen-bonded structure of the water unchanged,[11] and because the A^- and AL species may be expected[18] to have approximately the same effects on the water structure, *i.e.*, $(\gamma_{A^-})_\alpha/(\gamma_{A^-})_H = (\gamma_{AH})_\alpha/(\gamma_{AH})_H$. This reasoning is essentially the same as that employed in the derivation of the Gross equation[9,10,11b,15] the success of which in predicting rates and equilibria in aqueous acidic solutions is proven.

K_n' can be expressed from eq 3 and $K_{B,H}$ and $K_{B,D}$ from eq 5.

If it is assumed that the constant of the equilibrium

$$H_2O + D_2O \overset{K_{HDO}}{\rightleftharpoons} 2HDO \qquad (8)$$

has the statistical value of 4.0, the concentration of L_2O species in mole fractions can be expressed in terms of the deuterium atom fraction, α, as

$$N_{H_2O} = (1 - \alpha)^2;\ N_{HDO} = 2\alpha(1 - \alpha);\ N_{D_2O} = \alpha^2$$

After algebraic manipulations and appropriate substitutions, eq 9 results.

$$\frac{K_{B,\alpha}}{K_{B,H}} = (1 - \alpha)^2 + \frac{\alpha(1 - \alpha)}{K_n'} + \frac{K_{B,D}}{K_{B,H}}[K_n'\alpha(1 - \alpha) + \alpha^2] \qquad (9)$$

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The equilibrium constant of eq 8 is known to differ slightly from 4.0, having the value 3.76 at 25°.[20] Expressing the mole fractions of H_2O, HDO, and D_2O in terms of K_{HDO}, eq 10 results (for $0 < \alpha \leq 1$). K_n' can

$$N_{HDO} = \frac{K_{HDO} - \{K_{HDO}[K_{HDO}(2\alpha - 1)^2 + 16\alpha(1 - \alpha)]\}^{0.5}}{K_{HDO} - 4}$$

$$N_{D_2O} = \frac{2\alpha - N_{HDO}}{2}$$

$$N_{H_2O} = \frac{N_{HDO}^2}{K_{HDO}N_{D_2O}}$$

$$\frac{K_{B,\alpha}}{K_{B,H}} = N_{H_2O} + \frac{N_{H_2O}^{1/2}N_{D_2O}^{1/2}}{K_n'} + \frac{K_{B,D}}{K_{B,H}} \times [K_n'N_{H_2O}^{1/2}N_{D_2O}^{1/2} + N_{D_2O}] \quad (10)$$

be computed from the values of K_B in pure and mixed solvents. We obtained K_B values by measuring the dissociation constants of weak acids and the autoprotolysis constant of the solvent, since $K_{B,\alpha} = K_{L_2O,\alpha}/K_{A,\alpha}$.

Autoprotolysis of D_2O and D_2O–H_2O Mixtures. $K_{L_2O,\alpha}$ values at 25.0° and zero ionic strength have been obtained as described in the Experimental Section and are listed in Table I. These values can be described by eq 11, derived *via* the method of least-squares

$$\frac{K_{H_2O}}{K_{L_2O,\alpha}} = 1 + 2.4759\alpha - 3.1822\alpha^2 + 7.0176\alpha^3 \quad (11)$$

where $K_{H_2O} = 1.008 \times 10^{-14}\ M^2$. From eq 11, the autoprotolysis constant of D_2O, K_{D_2O}, is $1.379 \times 10^{-15}\ M^2$. Bates[8] and Gold[6] report very close agreement, 1.35×10^{-15} and 1.39×10^{-15}, respectively. The data (see Figure 1) are intermediate between those of Gold[6] and Long,[7] but closer to Gold's.

Table I. $K_{L_2O,\alpha}$ and $K_{H_2O}/K_{L_2O,\alpha}$ Values for Zero Ionic Strength at 25.0°

α	$K_{L_2O,\alpha} \times 10^{15}$, M^2		$K_{H_2O}/K_{L_2O,\alpha}$
0.997	1.383		7.288
0.997	1.390		7.252
0.997	1.390	av 1.389	7.252
0.997	1.382		7.294
0.997	1.398		7.210
0.797	2.249	av 2.252	4.482
0.797	2.256		4.468
0.597	3.517	av 3.506	2.866
0.597	3.495		2.884
0.398	5.138		1.962
0.199	7.381		1.366
0.000	10.07		1.001
0.000	10.08		1.000

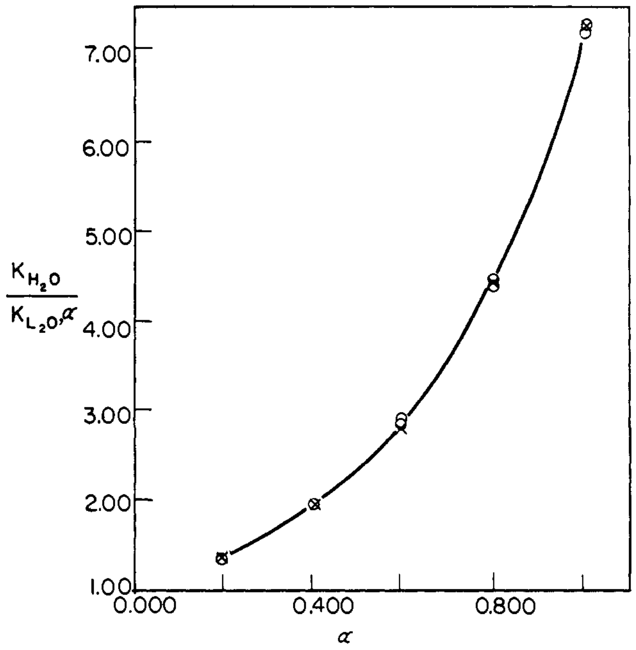

Figure 1. Autoprotolysis constant ratio of H_2O and mixed solvent as a function of atom fraction deuterium α: O, experimental; ×, calculated by least squares (eq 11).

Dissociation of Acids as a Function of Solvent Composition. The dissociation constant of a protio acid in H_2O is greater than that of the corresponding deuterio acid in D_2O, based on zero-point energy considerations.[21] The value of $\Delta pK = (pK_{A,D} - pK_{A,H})$ depends on the type of acid, and within the same type there is a small dependence on acid strength. Acids of higher ΔpK, *i.e.*, of higher $K_{B,D}/K_{B,H}$, allow the determination of K_n' with greater precision.

For 2,4-dinitrophenol, the reported ΔpK values are 0.52,[21b] 0.52,[22] 0.70,[23] 0.49,[24] and 0.56.[25] In this work, we have determined $pK_{A,\alpha}$ values for 2,4-dinitrophenol by spectrophotometric and pH measurements as shown in Table II.

Table II. Acid Dissociation Constants for 2,4-Dinitrophenol at Different Solvent Compositions at 25.0°

α	$pK_{A,\alpha}$	$K_{A,\alpha} \times 10^5$, M	$K_{A,\alpha}/K_{A,H}$
0.997	4.657	2.203	0.289
0.997	4.646	2.259	0.296
0.797	4.523	2.999	0.393
0.797	4.513	3.069	0.403
0.597	4.407	3.917	0.514
0.597	4.397	4.009	0.526
0.398	4.292	5.105	0.670
0.398	4.292	5.105	0.670
0.199	4.213	6.123	0.803
0.199	4.206	6.223	0.816
0.040	4.142	7.211	0.946
0.040	4.144	7.178	0.942
0.000	4.117	7.638	1.000
0.000	4.119	7.603	

The extrapolated value of $pK_{A,D}$ is 4.652; therefore, $\Delta pK = 0.53$.

For 2-nitrophenol the following ΔpK's have been reported: 0.57[21b], 0.75,[23] and 0.60.[25] We obtained $pK_{A,\alpha}$ values by half-neutralization point determinations as shown in Table III.

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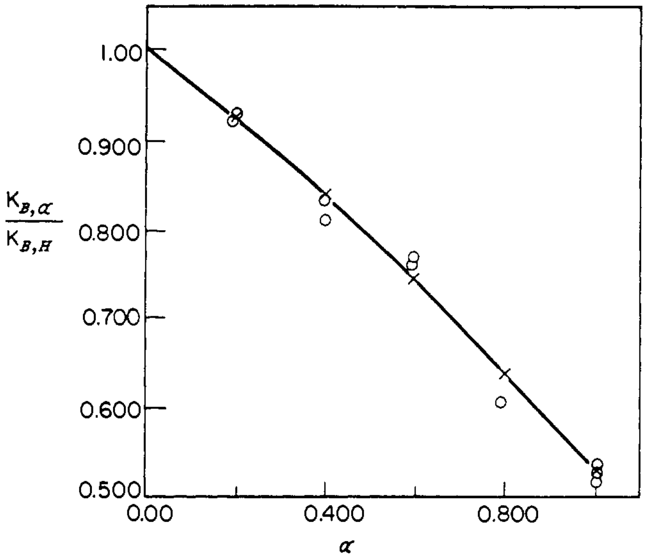

Figure 2. Isotope effect in the basic association of 2-nitrophenolate as a function of atom fraction deuterium α: ○, experimental; ×, calculated by least squares (eq 10).

Table III. Acid Dissociation Constants of 2-Nitrophenol for Different Solvent Compositions at 25.0°

α	$pK_{A,\alpha}$	$K_{A,\alpha} \times 10^8$, M	$K_{A,\alpha}/K_{A,H}$
0.997	7.810	1.549	0.265
0.997	7.813	1.538	0.263
0.997	7.823	1.503	0.257
0.797	7.669	2.143	0.366
0.597	7.575	2.661	0.455
0.597	7.572	2.679	0.458
0.398	7.447	3.573	0.611
0.398	7.433	3.690	0.631
0.199	7.335	4.624	0.791
0.199	7.333	4.645	0.794
0.000	7.233	5.848	1.000

The extrapolated value of $pK_{A,D}$ is 7.815; therefore, $\Delta pK = 0.58$.

The ΔpK of 0.53 for 2,4-dinitrophenol and 0.58 for 2-nitrophenol fall close to the straight line drawn through points representing various nitrophenols on a ΔpK *vs.* $pK_{A,H}$ plot. It appears that by considering zero-point energies, the dependence of ΔpK on pK is adequately accounted for.

Basic Association of Weak Bases. Determination of K_n'. $K_{B,\alpha}$ values for 2,4-dinitrophenolate and 2-nitrophenolate have been obtained from experimentally determined $K_{A,\alpha}$ and $K_{H_2O,\alpha}$ values and are listed in Table IV as $(K_{B,\alpha})_{obsd}$. With the aid of a computer program, calculations of the best least-squares fit to eq 10 adjusting the parameters K_n', K_{B,H_2O}, and K_{B,D_2O} were made. For 2-nitrophenolate a good fit was obtained, but for 2,4-dinitrophenolate the iterative procedure did not converge but oscillated around reasonable values of K_n'. Values of $(K_{B,\alpha})_{calcd}$ are given in Table IV; a plot for 2-nitrophenolate is given in Figure 2. The values of $(K_{B,\alpha})_{calcd}$ for 2,4-dinitrophenolate are based on eq 9, which gave convergence to a spurious value of K_n'. Identical values with those reported for 2-nitrophenolate were obtained with eq 9, but with a different value of K_n' than that obtained with eq 10. The computations were carried out on an IBM 7040 computer. The program was based on a generalized least-squares program developed by Lietzke.[26] Data from the literature on the dissociation of other acids also permitted computation of K_n' values.

Table IV. Basicity Constants of 2,4 Dinitrophenolate and 2-Nitrophenolate Ions for Different Solvent Compositions at 25.0°

	2,4-Dinitrophenolate		2-Nitrophenolate	
α	$[(K_{B,\alpha})_{obsd}] \times 10^{11}$, M	$[(K_{B,\alpha})_{calcd}] \times 10^{11}$, M	$[(K_{B,\alpha})_{obsd}] \times 10^{8}$, M	$[(K_{B,\alpha})_{calcd}] \times 10^{8}$, M
0.997	6.149	6.209	8.967	9.044
0.997	6.305		9.031	
0.997	. . .		9.241	
0.797	7.338	7.453	10.51	10.98
0.797	7.509		. . .	
0.597	8.745	8.795	13.17	12.76
0.597	8.951		13.09	
0.398	10.06	10.23	14.38	14.39
0.398	10.06		13.92	
0.199	11.86	11.76	15.96	15.88
0.199	12.05		15.89	
0.000	13.23	13.38	17.22	17.22

The dissociation of benzoic acid in D_2O–H_2O mixtures[21a] and the dissociation of acetic acid in D_2O–H_2O mixtures at zero ionic strength[27a] and at ionic strength 0.1[27b] have been studied. $(K_{B,\alpha})_{obsd}$ values for benzoic acid were obtained from the reported $K_{A,\alpha}$ values and from $K_{L_2O,\alpha}$ values determined in the present work (Table V); values for acetic acid at zero ionic strength were derived in a similar manner[27a] (acetic acid I, Table VI). For the acetic acid data at ionic strength 0.1,[27b] we extrapolated the values of $K_{L_2O,\alpha}$ to $I = 0.1$ assuming a linear dependence of log K on I. $(K_{B,\alpha})$ values then were obtained from the reported $K_{A,\alpha}$ and extrapolated $K_{L_2O,\alpha}$ values (acetic acid II, Table VII). Computations yielded values of $(K_{B,\alpha})_{calcd}$, K_n', K_{B,H_2O}, and K_{B,D_2O} for each of the three sets of data.

Table V. Basicity Constants of Benzoate Ion for Different Solvent Compositions at 25.0°

α	$[(K_{B,\alpha})_{obsd}] \times 10^{11}$, M	$[(K_{B,\alpha})_{calcd}] \times 10^{11}$, M
1.000	7.072	7.046
0.979	7.271	7.258
0.965	7.374	7.398
0.880	8.224	8.247
0.524	11.66	11.71
0.514	11.87	11.81
0.000	16.55	16.55

Table VI. Basicity Constants of Acetate Ion (Acetic Acid I) for Different Solvent Compositions at 25.0°

α	$[(K_{B,\alpha})_{obsd}] \times 10^{10}$, M	$[(K_{B,\alpha})_{calcd}] \times 10^{10}$, M
1.000	2.485	2.472
0.970	2.574	2.571
0.930	2.676	2.700
0.770	3.221	3.211
0.274	4.707	4.708
0.000	5.478	5.478

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Table VII. Basicity Constants of Acetate Ion (Acetic Acid II) for Different Solvent Compositions at 25°

α	$[(K_{B,\alpha})_{obsd}] \times 10^{10}$, M	$[(K_{B,\alpha})_{calcd}] \times 10^{10}$, M
1.000	1.236	1.256
0.988	1.228	1.274
0.969	1.327	1.303
0.925	1.475	1.372
0.919	1.415	1.382
0.819	1.452	1.536
0.785	1.547	1.587
0.745	1.644	1.648
0.556	1.950	1.930
0.351	2.260	2.227
0.264	2.341	2.351
0.259	2.379	2.358
0.098	2.535	2.583
0.000	2.737	2.718

A summary of K_n' values and of the basic association constants of 2,4-dinitrophenolate, 2-nitrophenolate, benzoate, and acetate ions in pure isotopic waters is given in Table VIII, along with the standard deviation of each coefficient.

Table VIII. Summary of Computed K_n' Values and Basicity Constants in Pure Isotopic Waters at 25.0°

Acid	K_{B,H_2O}, M	K_{B,D_2O}, M	K_n'	$K_{B,H_2O}/K_{B,D_2O}$
Benzoic acid	$(1.655 \pm 0.005) \times 10^{-10}$	$(7.046 \pm 0.027) \times 10^{-11}$	2.299 ± 0.046	2.28
Acetic acid I	$(5.478 \pm 0.016) \times 10^{-10}$	$(2.472 \pm 0.011) \times 10^{-10}$	2.224 ± 0.065	2.21
Acetic acid II	$(2.718 \pm 0.039) \times 10^{-10}$	$(1.256 \pm 0.025) \times 10^{-10}$	2.123 ± 0.261	2.17
2,4-Dinitrophenol[a]	$(1.338 \pm 0.014) \times 10^{-10}$	$(6.191 \pm 0.111) \times 10^{-11}$	1.671 ± 0.403	2.16
2-Nitrophenol	$(1.722 \pm 0.026) \times 10^{-7}$	$(9.014 \pm 0.174) \times 10^{-8}$	2.120 ± 0.190	1.91

[a] Results from eq 9; all others from eq 10.

The fact that 2,4-dinitrophenolate did not give a value of K_n' using eq 10 is not unreasonable, since there was a good deal of experimental scatter. In addition, there was probably a systematic error in the measurements: the experimental values of $K_{A,\alpha}/K_{A,H}$ at α = 0.398 and 0.597 are all higher than expected on the basis of the Gross equation. Any systematic error that might have occurred was probably associated with the ultraviolet measurements.

The precision of K_n' computed from the data on 2-nitrophenol is acceptable. Thus K_n' was found in this work to be 2.12 ± 0.19. K_n' values computed from literature data are in the region 2.30–2.12. In particular, the value for acetic acid II data, the only one of the three sets of literature data with a large number of points over a well-distributed range of atom fractions of deuterium, agrees very well with our 2-nitrophenol value (2.12 ± 0.26 *vs.* 2.12 ± 0.19).

In the absence of solvation isotope effects and, perhaps more importantly, if the isotopic fractionation in the O–L group of the acid is the same as that for a single O–L bond of L_2O, $K_{B,H_2O}/K_{B,D_2O}$ should be approximately equal to K_n' (*cf.* eq 5). This is very nearly true, as can be seen in Table VIII, the only marked deviation being for 2-nitrophenol. The other three acids are all of very nearly the same strength, while 2-nitrophenol is considerably weaker. The stronger acids would be expected, on zero-point energy arguments, to have isotope effects a little greater than K_n' (since their O–L bonds are presumably weaker than those of L_2O). The low isotope effect for 2-nitrophenol is explained, on the basis of zero-point energy effects, as resulting from its weaker acidity (stronger O–L bond than in the other three acids). It may also be noted that the value of K_n' calculated from our K_{H_2O}/K_{D_2O} value is 2.30 if l is assumed to be 0.68 (it would be somewhat greater for greater l).

Calculations with eq 9 gave comparable fits to those in Tables IV–VII, but with different values for K_n': 2.28, 2.48, 2.40, and 2.31 for 2-nitrophenolate, benzoate, acetate I, and acetate II, respectively.

Basic Association of Substrates with an Exchangeable Hydrogen. Equation 10 has been derived for the association of bases which contain no exchangeable hydrogen. In the mixed isotopic water solution of a base with one exchangeable hydrogen, the exchange equilibrium between protiated and deuterated forms must be taken into account.

Thus, the exchange equilibrium for imidazole, for example, is

$$\text{DIm} + {}^1\!/_2\text{H}_2\text{O} \overset{K}{\rightleftarrows} \text{HIm} + {}^1\!/_2\text{D}_2\text{O} \tag{12}$$

where HIm is the protiated and DIm the deuterated form of imidazole. A correlation between the isotope effect in the basic association and K_{B,H_2O}, K_{B,D_2O}, K_n', and K is derived as follows.

In the basic association of imidazole in mixed isotopic water solution the equilibria are established

$$\text{HIm} + \text{H}_2\text{O} \overset{K_{B,H}}{\rightleftarrows} \text{HImH}^+ + \text{HO}^-$$

$$\text{DIm} + \text{D}_2\text{O} \overset{K_{B,H}}{\rightleftarrows} \text{DImD}^+ + \text{DO}^-$$

$$\text{HIm} + \text{HDO} \rightleftarrows \text{HImD}^+ + \text{HO}^-$$

$$K_{B,H} = \frac{[\text{HImH}^+][\text{HO}^-]}{[\text{HIm}][\text{H}_2\text{O}]},\ K_{B,D} = \frac{[\text{DImD}^+][\text{DO}^-]}{[\text{DIm}][\text{D}_2\text{O}]}$$

$$K_\alpha = \frac{\{[\text{HImH}^+] + [\text{DImD}^+] + [\text{HImD}^+]\}\{[\text{HO}^-] + [\text{DO}^-]\}}{\{[\text{HIm}] + [\text{DIm}]\}\{[\text{H}_2\text{O}] + [\text{D}_2\text{O}] + [\text{HDO}]\}}$$

$$\frac{K_\alpha}{K_H} = \frac{\{[\text{HImH}^+] + [\text{DImH}^+] + [\text{DImD}^+]\} \times \{[\text{HO}^-] + [\text{DO}^-]\}[\text{HIm}][\text{H}_2\text{O}]}{\{[\text{HIm}] + [\text{DIm}]\} \times \{[\text{H}_2\text{O}] + [\text{HDO}] + [\text{D}_2\text{O}]\}[\text{HImH}^+][\text{HO}^-]} \tag{13}$$

Equation 13 can be rewritten as

$$\frac{K_\alpha}{K_H} = \frac{\left\{1 + \frac{[\text{DO}^-]}{[\text{HO}^-]}\right\}\left\{1 + \frac{[\text{HImD}^+]}{[\text{HImH}^+]} + \frac{[\text{DImD}^+]}{[\text{HImH}^+]}\right\}}{\left\{1 + \frac{[\text{DIm}]}{[\text{HIm}]}\right\}\left\{1 + \frac{[\text{HDO}]}{[\text{H}_2\text{O}]} + \frac{[\text{D}_2\text{O}]}{[\text{H}_2\text{O}]}\right\}}$$

From eq 12 the exchange equilibrium is expressed as

$$K = \frac{[\mathrm{HIm}][\mathrm{D_2O}]^{0.5}}{[\mathrm{DIm}][\mathrm{H_2O}]^{0.5}}$$

Since isotopic water and lyoxide ion concentrations can be expressed in terms of α and K_n', the concentration ratio of isotopic imidazole and imidazolium ions can be expressed as (assuming that $K_{\mathrm{HDO}} = 4$)

$$\frac{[\mathrm{DIm}]}{[\mathrm{HIm}]} = \frac{1}{K}\frac{\alpha}{1 - \alpha}$$

$$\frac{[\mathrm{DImD^+}]}{[\mathrm{HImH^+}]} = \frac{K_{\mathrm{B,D}}[\mathrm{DIm}][\mathrm{D_2O}][\mathrm{HO^-}]}{K_{\mathrm{B,H}}[\mathrm{HIm}][\mathrm{H_2O}][\mathrm{DO^-}]} = \frac{K_{\mathrm{B,D}}K_n'\alpha^2}{K_{\mathrm{B,H}}K(1 - \alpha)^2}$$

$$\frac{[\mathrm{HImD^+}]}{[\mathrm{HImH^+}]} = 2\left(\frac{K_{\mathrm{B,D}}K_n'}{K_{\mathrm{B,H}}K}\right)^{0.5}\frac{\alpha}{1 - \alpha}$$

The statistical factor 2 in the equation enters because $\mathrm{HImD^+}$ species are twice as probable as either $\mathrm{HImH^+}$ or $\mathrm{DImD^+}$ species. The square root follows from the application of the rule of geometric mean,[28] which for this case can be qualitatively expressed by stating that the fractionation factor for a species containing one D is the square root of the fractionation factor for a species containing two equivalent D's.

After substitutions, eq 14 results.

$$\frac{K_{\mathrm{B},\alpha}}{K_{\mathrm{B,H}}} = \frac{\left(1 + \frac{\alpha}{K_n'(1 - \alpha)}\right)}{\left(1 + \frac{\alpha}{K(1 - \alpha)}\right)} \times \left[1 + \left(\frac{K_{\mathrm{B,D}}K_n'}{K_{\mathrm{B,H}}K}\right)^{0.5}\frac{\alpha}{(1 - \alpha)}\right]^2(1 - \alpha)^2 \quad (14)$$

Equation 15 results if K_{HDO} is not assumed equal to 4 (*cf.* eq 10). If the value of the exchange constant K

$$\frac{K_{\mathrm{B},\alpha}}{K_{\mathrm{B,H}}} = \frac{1 + N_{\mathrm{D_2O}}{}^{0.5}/K_n'N_{\mathrm{H_2O}}{}^{0.5}}{1 + N_{\mathrm{D_2O}}{}^{0.5}/KN_{\mathrm{H_2O}}{}^{0.5}} \times \left[N_{\mathrm{H_2O}}{}^{0.5} + \left(\frac{K_{\mathrm{B,D}}K_n'}{K_{\mathrm{B,H}}K}\right)^{0.5}N_{\mathrm{D_2O}}{}^{0.5}\right]^2 \quad (15)$$

were known, K_n' could be computed from the change of isotope effect with solvent composition by means of eq 15. Conversely, eq 15 could be utilized to determine K if K_n' were known.

The acid dissociation constants of imidazolium ion have been determined by titration with HBr solution of the same solvent composition (see Table IX). Each number is an average of those calculated at three different degrees (0.25, 0.50, 0.75) of neutralization.

Table IX. Acid Dissociation Constants of Imidazolium Ion for Different Solvent Compositions at 25.0°

α	$\mathrm{p}K_{\mathrm{A},\alpha}$
0.997	7.469
0.997	7.476
0.797	7.352
0.797	7.351
0.597	7.252
0.597	7.245
0.398	7.150
0.398	7.141
0.199	7.054
0.000	6.978

The extrapolated value of $\mathrm{p}K_{\mathrm{A,D}}$ is 7.473; hence, $\Delta\mathrm{p}K = 0.50$. $(K_{\mathrm{B},\alpha})_{\mathrm{obsd}}$ values for imidazole have been obtained from the experimentally determined values of $K_{\mathrm{A},\alpha}$ and $K_{\mathrm{L_2O},\alpha}$ (see Table X). The best fit of eq 15 to these was computed by assuming, in the first approximation, that $K = 1.00$, and these values are quoted in Table X. The following parameters resulted: $K_{\mathrm{B,H}} = (9.557 \pm 0.043) \times 10^{-8}$, $K_{\mathrm{B,D}} = (4.093 \pm 0.035) \times 10^{-8}$, and $K_n' = 1.819 \pm 0.112$. Bases with no exchangeable hydrogen, however, gave higher values for K_n'; therefore, K may be different from unity. Assuming $K_n' = 2.120$, the fit of the data with $K = 1.00$ is very little worse than with $K_n' = 1.819$. In attempting to determine the value of K which gave the best fit, it was found that a very shallow minimum occurred with K_n' *ca.* 2.1 and K *ca.* 0.75, which we believe to be a spuriously low value for K.

Table X. Basicity Constants of Imidazole for Different Solvent Compositions at 25.0°

α	$[(K_{\mathrm{B},\alpha})_{\mathrm{obsd}}] \times 10^8$, M	$[(K_{\mathrm{B},\alpha})_{\mathrm{calcd}}] \times 10^8$, M
0.997	4.090	4.107
0.997	4.156	. . .
0.797	5.065	5.100
0.797	5.053	. . .
0.597	6.263	6.141
0.597	6.164	. . .
0.398	7.257	7.226
0.398	7.108	. . .
0.199	8.358	8.363
0.000	9.564	9.557
0.000	9.564	. . .

Experimental Section

Water. Carbon dioxide free conductivity water was used in all experiments. $\mathrm{D_2O}$ was purchased from General Dynamics Corp., minimum purity 99.7%. $\mathrm{D_2O}$ was boiled before use and the deuterium atom fraction was 0.997 as determined by nmr.

Reagent grade chemicals were recrystallized several times to constant melting points. The melting points are uncorrected. 2,4-Dinitrophenol was recrystallized from conductivity water, mp 112.5°. Imidazole was recrystallized from dry benzene, mp 89.5°. 2-Nitrophenol was recrystallized from conductivity water, mp 45.6°.

$\mathrm{H_2O}$ and $\mathrm{D_2O}$ solutions of strong base and acid were prepared in a nitrogen-filled drybox. NaOH and NaOD solutions were prepared from sodium and water. Stock solutions were diluted and standardized against benzoic acid solutions. Benzoic acid was obtained from the National Bureau of Standards. HBr and DBr solutions were prepared from gaseous hydrogen bromide with vacuum-line techniques. For $\mathrm{D_2O}$ solutions, the glassware and electrode cell were baked in an oven at 220° for several hours.

Solutions in mixed solvents were prepared from solutions in pure isotopic waters. Each substrate was studied in four $\mathrm{D_2O}$-$\mathrm{H_2O}$ mixtures containing 80, 60, 40, and 20 vol. % of the $\mathrm{D_2O}$ solution at 25°. The corresponding deuterium atom fractions are 0.797, 0.597, 0.398, and 0.199, respectively.

pH Measurements. A Radiometer pH meter-automatic titrator, Type TTT1C, was used, in conjunction with a scale expander, Type PHA 630 Ta. pH values were read directly to two decimals; the third decimal was estimated. The electrodes were Radiometer G 202 B glass electrode and K 401 calomel electrode.

A jacketed electrode cell was used, the temperature of which was maintained constant by circulating water through the jacket from a constant-temperature bath thermostated at 24.98 ± 0.05°.

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[28] J. Bigeleisen, *J. Chem. Phys.*, 23, 2264 (1955); in view of the fact that K_{HDO} differs from 4.0 by *ca.* 7%,[20] this rule is now considered to be somewhat approximate (probably less approximate for the larger imidazolium ion than for water, however). This approximation was intuitively applied by P. Gross, *Z. Elektrochem.*, **44**, 299 (1938).

The cell was swept with a slow nitrogen stream during titrations. Solutions were stirred with a magnetic stirring bar coated with Kel-F. All CO_2-sensitive solutions and all D_2O solutions were pipeted into the electrode cell inside the drybox.

The pH meter was standardized with buffers, obtained from the National Bureau of Standards. Buffer solutions were prepared as described by Bates.[29] The standardization was carried out with two buffers, different by several units of pH, thus ensuring linear response of the glass electrode.

Determination of Autoprotolysis Constants. The autoprotolysis constants of pure and mixed isotopic waters, K_{L_2O}, were determined by measuring the OL^- and L_3O^+ concentration of a base solution. In order to read acidity in D_2O solutions, the pH meter scale must be calibrated in terms of L_3O^+ activity. The calibration correction, ΔpH_{L_2O}, was obtained with a solution of known L_3O^+ activity.

$$\Delta pH_{L_2O} = (-\log [L_3O^+] + \text{activity correction}) - (\text{meter reading}_{L_2O})$$

DBr solutions (0.01 and 0.001 *M*) in heavy water and their mixtures with 0.01 and 0.001 *M* HBr in H_2O were employed. The precision of the measurements was estimated to be ±0.003 pH unit.

The activity corrections were determined empirically for H_2O solutions and applied to all mixtures of the same acid concentration. The following activity correction values have been measured, where activity correction = meter reading − (−log $[H_3O^+]$): 0.001 *M* HBr, 0.069, 0.070; 0.01 *M* HBr, 0.066, 0.066, 0.064, 0.070, 0.070. The ΔpH_{L_2O} values are listed in Table XI. From these experimental values, the equation

Table XI. ΔpH_{L_2O} at 25°

α	ΔpH_{L_2O}[a] 0.01 *M* HBr	ΔpH_{L_2O}[a] 0.001 *M* HBr
0.997	0.396, 0.392	0.401
0.797	0.302, 0.299	0.314
0.597	0.211, 0.216	0.230
0.398	0.139, 0.138	0.152
0.199	0.055, 0.063	0.058

[a] (pH meter reading in H_2O) − (pH meter reading in mixed solvent).

$$\Delta pH_{L_2O} = 0.3139\alpha + 0.0854\alpha^2$$

was derived by the method of least squares. From the equation the following ΔpH_{L_2O} values have been computed for the solvent compositions employed (α, ΔpH_{L_2O}): 0.199, 0.066; 0.398, 0.138; 0.597, 0.218; 0.797, 0.304; 0.997, 0.398. These values have been employed in subsequent calculations.

The activity correction has also been determined in 0.01 and 0.001 *M* NaOH solution: 0.001 *M* NaOH, activity correction = 0.085; 0.01 *M* NaOH, activity correction = 0.118. The calibration correction, ΔpH_{D_2O}, has been measured in NaOD solutions (α = 0.997): 0.001 *M* NaOD, ΔpH_{D_2O} = 0.399; 0.01 *M* NaOD, ΔpH_{D_2O} = 0.392. The values of the calibration correction obtained in basic solutions agree well with those obtained in acidic solutions. The values are constant and reproducible, even though the activity corrections used in calculating them are experimental figures and are not in agreement with those derived from the Debye–Hückel equation (0.016 for 0.001 *M* and 0.047 for 0.01 *M* solutions). Considerations of liquid junction potentials and electrode errors failed to account satisfactorily for the discrepancy. The interpretation is especially difficult in the case of acidic solutions, where the activity correction was found to be within experimental error for 0.001 and 0.01 *M* solutions.

The experimentally determined activity corrections, however, were reproducible and were accepted and utilized as obtained for the calculation of the calibration corrections.

For example, in 0.01 *M* DBr solution (α = 0.997) the deuterium ion concentration by titration was $[D_3O^+]$ = 0.00933 *M*; −log $[D_3O^+]$ = 2.030; activity correction = 0.066; pH meter reading = 1.700. Hence, $\Delta pH_{\alpha = 0.997}$ = 2.030 + 0.066 − 1.700 = 0.396.

To determine the autoprotolysis constant of an aqueous isotopic mixture, L_2O, a sample of a 0.01 or 0.001 *M* NaOL solution was titrated, the OL^- concentration determined, and a reading on the pH meter taken.

$$K_{L_2O} = a_{L^+} \times a_{OL^-}$$

where a_{L^+} = antilog [−(meter reading + pH_{L_2O})] and a_{OL^-} = $[LO^-]$[antilog(−activity correction)]. For example, in 0.01 *M* NaOD solution (α = 0.997) the deuterioxide ion concentration by titration was $[OD^-]$ = 0.01073 *M*; pH meter reading = 12.381; activity correction = 0.118; pD = 12.381 + 0.398 = 12.779.

$$K_{\alpha = 0.997} = [\text{antilog}(-12.779)] \times [0.01073\ \text{antilog}(-0.118)] = 1.361 \times 10^{-15}$$

The autoprotolysis constant of H_2O as a function of ionic strength has been determined.[30] Since activity coefficients due to salt effects in aqueous solvents change with solvent composition insignificantly,[31] K_{L_2O} values were extrapolated to $I = 0$, making use of the known K_{H_2O} *vs.* *I* relationship. Thus the above-derived $K_{\alpha = 0.997}$ at $I = 0$ equals 1.383×10^{-15}.

p*K* Determinations of 2,4-Dinitrophenol. Unbuffered aqueous solutions (1.1×10^{-4} *M*) were used. For each solvent composition, the pH meter reading was taken and the absorbance of the solution at 390 mμ was determined. The value of pK_A in solvent L_2O was calculated from the equation

$$pK_{A,\alpha} = pH - \log \frac{(D - D_1)}{(D_2 - D)} - \log \gamma_{R^-} + \Delta pH_\alpha$$

where $pK_{A,\alpha}$ = thermodynamic acid dissociation constant in solvent of composition α, pH = meter reading, ΔpH_α = calibration correction, D_1 = absorbance of undissociated phenol, D_2 = absorbance of phenoxide, D = absorbance of phenol solution to be analyzed containing both phenol and phenoxide, and γ_{R^-} = activity coefficient of phenoxide = $0.5108I^{0.5}/(1 + 1.5I^{0.5})$. The activity coefficient of undissociated phenol is assumed to be 1.0. For example, at α = 0.398, pH meter reading = 4.403; average reading of absorbances, D = 0.792, D_1 = 0.027, D_2 = 1.222; ΔpH_α = 0.138; $-\log \gamma_{R^-}$ = 0.001; $pK_{A,\alpha = 0.398}$ = 4.403 − 0.250 + 0.138 + 0.001 = 4.292. A Perkin-Elmer ultraviolet–visible spectrophotometer, Model 202, was used with matching Beckman quartz cells of 1-cm path length. The cells were placed in a "Controlled temperature cell mount 220-0089." Water from the thermostated bath circulated through the cell mount.

p*K* Determinations of 2-Nitrophenol. 2-Nitrophenol solutions (0.002 *M*) in pure light and heavy water and in their mixtures were titrated with 0.01 *M* NaOL solution of the same solvent composition and pK_A's were calculated from the equation

$$pK_{A,\alpha} = pH - \log \gamma_{R^-} + \Delta pH_\alpha$$

where the pH was read from the titration curve at half-neutralization. The neutralization point was determined from a log (ΔpH/Δml) *vs.* ml plot. For example, at α = 0.398 the inflection point of the titration curve was at 1.365 ml of added base; pH meter reading at half-neutralization = 7.280; $-\log \gamma_{R^-}$ = 0.015; hence, $pK_{A,\alpha = 0.398}$ = 7.280 + 0.015 + 0.138 = 7.433.

p*K* Determinations of Imidazole. pK_A values were determined by half-neutralization point measurements in H_2O at various ionic strengths by titrating 0.01 *M* solutions with 0.04 *M* HBr solution. The experimentally determined pK_A's and their values at $I = 0$ are given in Table XII. The activity coefficients were calculated from the Debye–Hückel equation.

Table XII

I	0.006	0.040	0.10	0.20	0.50
pK_{A,H_2O}	7.015	7.052	7.102	7.129	7.174
$pK_{A,H_2O}(I = 0)$	6.980	6.973	6.993	6.992	6.999

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(29) R. G. Bates, *J. Res. Natl. Bur. Std.*, **66A**, 179 (1962).

(30) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1958, p 638.

(31) See ref 2, p 46.

In D_2O and D_2O–H_2O solutions, the 0.25, 0.50, and 0.75 neutralization points were determined from each titration. The ionic strength of the solutions was set to 0.04 with KCl. $pK_{A,\alpha}$ values were calculated from the equation

$$pK_{A,\alpha} = pH - \log \frac{[Im]}{[Im^+]} + \log \gamma + \Delta pH_\alpha$$

For example, at $\alpha = 0.398$ the inflection point of the titration curve was at 3.800 ml of added acid; pH meter reading at 0.25 neutralization point, 7.563, at 0.5, 7.085, at 0.75, 6.597; $-\log \gamma = 0.079$; hence $pK_{A,\alpha=0.398} = 7.563 - 0.477 + 0.138 - 0.079 = 7.145$; $= 7.085 + 0.138 - 0.079 = 7.144$; $= 6.597 + 0.477 + 0.138 - 0.079 = 7.133$; av 7.141.

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Secondary Isotope Effects in the Solvolysis of Norbornyl Bromides

John P. Schaefer, Michael J. Dagani, and David S. Weinberg

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona. *Received August 1, 1967*

Abstract: Optically active deuterated norbornyl bromides were prepared and their solvolyses were studied. The following secondary isotope effects (k_H/k_D) per D were observed or calculated: 3,3-d_2-*exo*-norbornyl bromide, 1.04 (polarimetric), 1.02 (titrimetric); 7,7-d_2-*exo*-norbornyl bromide, ~1.0; 3,3-d_2-*endo*-norbornyl bromide, 1.16; 2-*d*-*endo*-norbornyl bromide, 1.28. An analysis of these results suggests that, in the solvolysis of *endo*-norbornyl bromide, the degree of bond breaking which has occurred at the transition state is abnormally large. It is suggested that this is a result of unfavorable steric interactions between the departing halide and the C_6 methylene group. The strikingly low isotope effects observed in the *exo* series are consistent with the proposal that the transition state for the ionization of *exo*-norbornyl derivatives is delocalized and nonclassical. However, the absence of a detectable isotope effect from the 7 position suggests that the geometry of the norbornyl skeleton has not yet undergone a major change at this stage.

The nature of the norbornyl cation and of the transition states that lead to this ion in a spectrum of reactions[1–10] is unquestionably one of the most stimulating problems with which organic chemists have concerned themselves. The extensive literature pertaining to this problem has been critically reviewed[11,12] and the majority of the workers in the field appear to favor giving the existing data interpretations that involve transition states that incorporate σ- or π-bond participation and lead to a nonclassical ion. Brown[13] and his co-workers have vigorously challenged these viewpoints and have precipitated further studies in this area.

The facts on which the postulate that the solvolysis of *exo*-norbornyl derivatives is assisted and leads to a bridged ion is based are high *exo*/*endo* ratio of ionization rates,[1,2] the stereochemical fate of the cation, namely, racemization,[1,2] a pronounced preference for *exo* addition,[2] and formation of nortricyclene rather than norbornene upon eliminaton.[2,5] Brown,[13] however, has contended that these observations are insufficient to require a nonclassical ion and has suggested that the data can also be accommodated by a pair of rapidly equilibrating ions in which steric factors control the ultimate fate of the ions.

The bulk of recent data[11] that purport to concern the norbornyl cation has been obtained by modifying the norbornyl skeleton and studying the effect of these alterations on the reactivity of the system. Although these data are of interest, their value in resolving the basic problem is obscured by the fact that the drastic changes that are frequently made (*e.g.*, conversion of a secondary to a tertiary center) may upset the delicate balance of factors that exist in the parent system. In addition, new deriving forces that may bear no resemblance to those influencing the reactivity of norbornyl compounds are introduced by these changes. Since isotopic substitutions are the most subtle variations that can be made in a molecule, we have initiated a detailed investigation of the effect of isotopic substitution on the reactivity of norbornyl compounds in an effort to obtain additional data pertaining to the parent system and to the transition state that leads to the norbornyl cation.

If the features of the transition state for the ionization of *exo*-norbornyl tosylate as depicted by Winstein and

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