assumed to be equal to kT/h on the basis of Eyring's theory,[14] then $K_{SD^+}/K_{SH^+} = 2.35$.

The increase in the rate on passing to the deutero catalyst is thus explained as the result of a shift in the equilibrium in favor of the heavy complex. We must, however, note that although Urey and Rittenberg[15] have calculated that the equilibrium constant for the reaction $H_2 + 2DCl = 2HCl + D_2$ is shifted in favor of DCl, the reverse was found for $H_2 + 2DI = 2HI + D_2$. The position of the equilibrium $CH_3COCH_3 + HDO = CH_3COCH_2D + H_2O$ was measured by Halford, Anderson and Bates[16] and they found that the equilibrium constant is about two in favor of formation of heavy acetone.

Conclusions

1. The kinetics of the hydrogen-ion catalyzed hydrolysis of ethyl orthoformate in acetic acid–sodium acetate buffers of constant ratio has been investigated over the entire range of H_2O–D_2O mixtures.

2. The specific catalytic constant for D_3O^+ ion is 2.35 times greater than for H_3O^+.

3. A semi-micro dilatometer was constructed for the kinetic measurements which yields results in excellent agreement with the macro results of Harned and Samaras in H_2O.

4. An equation, from which the concentration of hydrogen and deuterium ions can be calculated, is derived.

5. The rate constant for constant acid/salt ratio decreases with increasing D content and shows a negative deviation from linearity. The sum $(C_{H^+} + C_{D^+})$ follows a similar curve. The specific rate constant or catalytic coefficient increases with increasing D content, and is linear with respect to the fraction of deuterium ions.

6. The calculated dissociation constants of a weak acid in H_2O–D_2O mixtures, defined as $(C_{H^+} + C_{D^+})C_{A^-}$/Total undiss. acid, are in substantial agreement with values obtained from the conductance method.

7. The greater catalytic effect of D^+ ion is explained as a shift in the equilibrium $S + H^+ \rightleftarrows SH^+$ in favor of the deutero complex in agreement with Bonhoeffer's treatment.

NEW YORK, N. Y. RECEIVED MARCH 22, 1938

[14] Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

[15] Urey and Rittenberg, *ibid.*, **1**, 137 (1933).

[16] Halford, Anderson and Bates, THIS JOURNAL, **56**, 491 (1934); *ibid.*, **57**, 1663 (1935); see also Wirtz, *Z. physik. Chem.*, **B34**, 121 (1936); *Z. Elektrochem.*, **43**, 662 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Temperature Coefficients of the Base Catalyzed Decomposition of Nitramide in Deuterium Oxide

BY SILVESTER LIOTTA AND VICTOR K. LA MER

The basic decomposition of nitramide ($H_2N_2O_2$) to nitrous oxide and water is catalyzed by the presence of any molecule, for example, water or the anions of weak acids, which possesses the property of associating a proton; *i. e.*, by basic molecules in the Brönsted formulation. The molar catalytic constant, k, is related to the dissociation constant, K_A, of the acid, conjugate to the catalyst base, by the well-known empirical formula $G = kK_A^{\alpha}$. For carboxylic anions in water, $\alpha = 0.83$, indicating a high sensitivity of the substrate to changes in K_A. Since deuterium substitution always reduces the value of K_A by a factor of 2 to 4, depending upon the strength and type of the acid, it becomes of interest to investigate the effect of deuterium substitution upon the rate of anion catalysis by determining the effect upon the constant G and the sensitivity index α.

It is also one of the purposes of this investigation to study in how far the rate depressing action of deuterium substitution arises from a displacement of the energy of activation and of the entropy of activation.

When proto nitramide is dissolved in D_2O at least one and presumably both protons are exchanged instantaneously for deutons, producing deutero-nitramide as the effective substrate.[1] In their investigation of the effect of deuterium substitution upon the *solvent catalysis*, La Mer and Greenspan[2] found that the substitution of deuterium for protium in the solvent produced a 5.21-fold decrease in rate.

There are two possible mechanisms. The first, suggested by Brönsted and supported by Peder-

[1] Unpublished measurements of Hochberg in this Laboratory. See La Mer, *Trans. Faraday Soc.*, **34**, 263 (1938).

[2] La Mer and Greenspan, *ibid.*, **33**, 1266 (1937).

sen and by Marlies and La Mer, postulates that the rate-determining step is the rate of transfer of the proton from the substrate to the catalyst base. The slower rate in D_2O on this mechanism would be ascribed to the slower rate of donation and of acceptance of deutons as compared to protons.

The second, based upon the transition state theory of kinetics, would ascribe the difference in rate on passing from the proto to the deutero systems to a shift in the equilibrium between reactants and critical complex with the additional possibility of a differential rate of decomposition of the proto and deutero complexes.

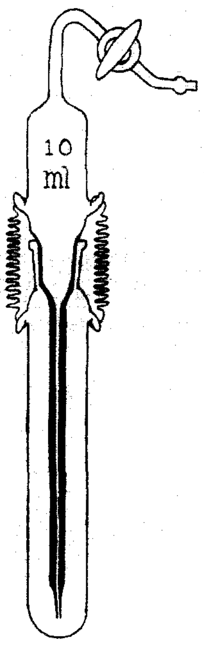

Fig. 1.—Special weight pipet.

If one employs anions like acetate, benzoate and salicylate rather than the solvent as the effective catalyst base, the problem becomes somewhat simplified since the hydrogens attached to carbon do not exchange and the base remains unchanged regardless of the D content of the solvent. For a more detailed treatment of the general problem of isotopic exchange and the effects of deuterium substitution for hydrogen upon the properties of conductance, e. m. f. and acid-base catalysis the reader is referred to current reviews and symposia.[3]

The difficulty of obtaining sufficiently large quantities of water with high deuterium content when this investigation was initiated (1935) led to the development of a gas evolution apparatus[4] applicable to a precision study on a semi-micro scale. The apparatus, which requires only 10 cc. of solution, yields results which are even more precise than those obtained with the macro-types employing 60–100 cc. of solution.

Preparation of Materials

Nitramide was prepared by the improved method of Marlies and La Mer.[5]

Heavy water was initially purified by distillation at atmospheric pressure from alkaline permanganate, from acid chromate and finally vacuum distilled in an all-glass Pyrex still with a receiver cooled with solid carbon dioxide-alcohol mixture. The water was recovered by vacuum distillation after neutralization of excess acid with solid sodium hydroxide. After each cycle of use, neutralization and distillation, the deuterium content diminished by only 0.2%.

Sodium acetate was recrystallized from distilled water, and dried *in vacuo* over calcium chloride at 40° for three days. Complete dehydration was achieved in two days at 115° following a gradual elevation of temperature to prevent fusion of the hydrate. The purity of the reagents was established by kinetic comparisons with the values of k_{Ac^-} and k_{H_2O} obtained in H_2O by previous investigators.

Acetic acid was prepared by adding acetic anhydride directly to the H_2O–D_2O solvent. The anhydride was triply distilled in a Pyrex Vigreux fractionating column, retaining as the final fraction the distillate boiling at 139.0 ± 0.1°.

Sodium benzoate and sodium salicylate were recrystallized twice from distilled water; **benzoic acid** twice from alcohol; **salicylic acid** twice from chloroform. All salts were dried in a vacuum desiccator.

The solutions were made up just before use by weighing acid, salt and solvent in the same container. Acetic anhydride and sodium acetate were added with a special weight pipet (Fig. 1). The latter was added in the form of a concentrated solution of known composition.

Apparatus and Experimental Procedure

The semi-micro apparatus contains a number of specific improvements which have been described in detail elsewhere. Four such instruments were immersed in a thermostat maintained within ± 0.004° at 15°, ± 0.002° at 25° and ± 0.003° at 35°, and checked against a B. S. standardized platinum resistance thermometer.

Since the decomposition yields only a few milligrams of H_2O and N_2O as the sole products, the composition of the solution is changed only by a small calculable decrease in D content and should, therefore, be available for successive runs without removal from the apparatus or variation in the concentration of the catalyst. This procedure was highly satisfactory in the previous work where hydrochloric acid solutions were involved but failed in the case of the sodium acetate solutions.

The conflicting reports in the literature on isotopic exchange with acetate ion naturally suggested that we were observing the effects of slow exchange of H by D on the carbons of the acetate ion. Specially designed experiments, however, established that no exchange takes place at 25° over two weeks' time since the densities of the recovered waters in these experiments remained constant to within five parts in 100,000.[6] The disturbance was finally traced to the instability of dilute sodium acetate–acetic acid buffers,[7] very likely through bacterial decomposition. This conclusion was confirmed by measuring the change in conductance with time, of a representative solution of 0.01 *M* sodium acetate and 0.04 *M* acetic acid with the following results

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[3] Symposium on proton transfers, *Trans. Faraday Soc.*, **34**, 229–265 (1938); Symposium on Deuterium, *Z. Elektrochem.*, **44** (Jan., 1938). Papers by Reitz p. 72 and Schwarzenbach p. 46; La Mer, *Chem. Rev.*, **19**, 363 (1936); Wynne-Jones, *ibid.*, **17**, 115 (1935).

[4] Greenspan, La Mer and Liotta, THIS JOURNAL, **59**, 1606 (1937).

[5] Marlies and La Mer, *ibid.*, **57**, 2008 (1935).

[6] Liotta and La Mer, *ibid.*, **59**, 946 (1937); Ives, *J. Chem. Soc.*, 81 (1938).

[7] MacInnes and Shedlovsky, *ibid.*, **54**, 1431 (1932); Chase, *ibid.*, **55**, 3072 (1933).

Time, days	0	1	2	3	5
Resistance, ohms	683	681	679	678	675

When the buffer solutions were prepared and used immediately thereafter, reproducible results were always obtained, which procedure was accordingly adopted.

Methods of Calculation

The anion catalyzed decomposition follows accurately the first order law in heavy water mixtures. Since the final pressure is proportional to the initial concentration (C_0) and the instantaneous concentration (C_1) is proportional to the difference between the final and instantaneous pressures

$$k^* = (1/t) \ln (p_\infty - p_0)/p_\infty - p) \qquad (1)$$

$$\text{or } \log (p_\infty - p) = \text{const.} - kt \qquad (2)$$

where $k = 0.4343\ k^*$.

The units of time and concentration are minutes and moles per liter, respectively. The graphical determination of k from $\log (p_\infty - p)$ *versus* t plots is too cumbersome and not sufficiently precise to warrant its use. An especially simple analytical method based on the principles of least squares, if the observations are separated by equal time intervals, suggested by Roeser,[8] has been found satisfactory by Marlies and La Mer.[9] This method gave the best agreement between independent experiments.

Unless the reaction requires an exceedingly long time for completion, p_∞ should be the most accurate measurement of the series since the readings can be repeated. Practically, however, the possibility of leaks in the apparatus or of side reactions like the decomposition of the buffer, require the use of the Guggenheim method[10] when the end-point cannot be determined more precisely than the running values of p. We found this method to be better for the exceedingly slow spontaneous decomposition at 15°.

The molar catalytic constant k is obtained from the relation $k = (k_{\text{obsd.}} - k_0)/C$, where k_0 is the velocity of the spontaneous decomposition due to the solvent and C is the concentration of the catalyst in moles per liter. When 0.01 M hydrochloric acid is used, $k_{\text{obsd.}}$ yields k_0 directly. The hydrochloric acid serves to eliminate the presence of hydroxyl ion and since at that concentration the acid catalysis is negligible, the rate is entirely due to the basic properties of the solvent. In this work we were obliged to use water of D content = 91.5% rather than 100% D_2O so that the respective catalytic constants are made up of two factors, the major part due to the 91.5% D_2O and a small part to the 8.5% H_2O.

Experimental Results

The values obtained for $k_{\text{obsd.}}$ and k are given in Table I. Variation in anion and acid concentration produced no variation in molar catalytic constant k. The values of the temperature coefficients for 15–25°, the energies of activation E and the frequency factor B in the integrated form of the Arrhenius equation

$$\log k = B - \frac{E}{2.3RT} \qquad (3)$$

are given in Table II. The values for H_2O were obtained by Baughan and Bell,[11] who use a least square treatment over a range of temperature. In Table III are listed the values of k at 15 and 25° as well as their ratios in the two solvents.

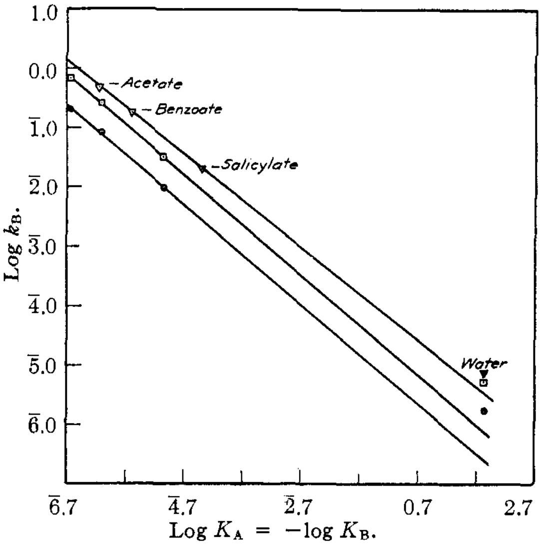

Fig. 2.—The relation between the logarithms of the velocity constants (ordinates) and dissociation constants (abscissas): ▽, H_2O at 15°; □, D_2O at 25°; ○, D_2O at 15°.

Discussion

Rate and Equilibrium Constants.—Brönsted's equation for generalized base catalysis

$$\log k_B = \log G - \alpha \log K_A \qquad (4)$$

is tested at F_D = 91.5% in Fig. 2 by plotting $\log k_B$ against $\log K_A$. The three anion bases chosen extend over a range of 1.4 units in log k and 1.6 units in log K_A. Since the acidic dissociation constants in D_2O at 15° were not all

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(8) Roeser, *Bur. Standards Bull.*, **16**, 363 (1920) (Sci. paper 388).

(9) Marlies and La Mer, THIS JOURNAL, **57**, 1812 (1935).

(10) Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

(11) Baughan and Bell, *Proc. Roy. Soc.* (London), **158**, 464 (1937).

TABLE I

SUMMARY OF THE KINETIC DATA

Temp., °C.	Salt	%D = $\left(\frac{\Delta S}{0.1079} \times 100\right)$	C_{acid}	C_{anion}	$k_{obsd.} \times 10^5$	k	Mean k	k corr. to 15, 25 or 35°
15.066	Acetate	91.56	0.0392	0.1754	400	0.2030	0.2060	0.2042
			.0392	.1754	405	.2056		
			.0392	.01278	305.5	.2096		
15.077	Benzoate	91.28	.00734	.01247	125.4	.0845	.0823	.0816
			.00734	.01247	122.1	.0821		
			.00338	.00946	95.46	.0825		
			.00338	.00946	93.15	.0803		
15.078	Salicylate	91.10	.00816	.01855	29.40	.00955	.00963	.00954
			.00816	.01855	29.70	.00969		
			.00544	.01927	30.93	.00991		
			.00544	.01927	29.79	.00938		
15.077	Spontaneous	91.28	.01 HCl		9.23		100×10^{-6}	99×10^{-6}
					10.78			
24.893	Acetate	91.66	.0392	.004206	362.0	.722	0.719	0.728
			.0392	.004206	362.4	.723		
			.0392	.004816	408.2	.718		
			.0392	.004816	404.9	.712		
24.884	Benzoate	90.92	.00317	.00903	288.3	.262	.261	.264
			.00317	.00903	287.5	.261		
			.00493	.01432	440.8	.262		
			.00493	.01432	435.6	.259		
24.881	Salicylate	90.92	.00430	.01953	98.36	.0322	.0323	.0328
			.00422	.01839	95.03	.0326		
			.00422	.01839	94.30	.0322		
24.89	Spontaneous	91.5	Interpolated[2]		30.04		300×10^{-6}	304×10^{-6}
34.966	Spontaneous	90.84	0.01 HCl		94.35		949×10^{-6}	953×10^{-6}
					94.82			
					95.24			
					95.27			

TABLE II

	H_2O				D_2O (91.5%)			
Catalyst	$k_{25°}/k_{15°}$	B	E	$\log k^{25°}_{H_2O}$	$k_{25°}/k_{15°}$	B	E	$\log k^{25°}_{D_2O}$
Acetate	3.01	14.25	19,180	$\bar{0}.1703$	3.57	15.80	21,726	$\bar{1}.862$
Benzoate	2.91	13.89	19,260	$\bar{1}.740$	3.24	14.15	20,082	$\bar{1}.422$
Salicylate	3.18	13.56	20,080	$\bar{2}.823$	3.44	14.00	21,101	$\bar{2}.516$
Spontaneous	3.20	12.28	20,680	$\bar{3}.088$	3.07 3.13 (25–35°)	11.16 (15–35°)	19,974 (15–35°)	$\bar{4}.483$

TABLE III

D_2O refers to 91.5% D content

Catalyst	$k^{15°}_{H_2O}$ (11)	$k^{15°}_{D_2O}$	$k^{25°}_{H_2O}$ (11)	$k^{25°}_{D_2O}$	k_{H_2O}/k_{D_2O} (15°)	k_{H_2O}/k_{D_2O} (25°)
Acetate	0.492	0.204	1.480	0.728	2.416	2.04
Benzoate	.183	.0816	0.550	.264	2.25	2.09
Salicylate	.0209	.00954	.0665	.0328	2.20	2.03
Spontaneous	383×10^{-6}	99×10^{-6}	1225×10^{-6}	$304. \times 10^{-6}$	3.86	4.02[a]

[a] Using Greenspan's more precise value for $k_0^{25°} = 1266 \times 10^{-6}$, then $k_{H_2O}/k_{D_2O} = 4.12$.

available, the use of values of K_A measured at 25° may account for the minor discrepancies from linearity on the 15° curve.

In heavy water as well as in light water, the point representing the catalytic properties of the solvent acting as a base lies above the continuation of the line obtained with the anion bases. This is consistent with Pedersen's theory[12] that for bases of the same strength the catalytic effect increases in the series $B^- < B^0 < B^+$ provided the substrate is uncharged. The difference may also arise from the fact that H_2O is a base of a different chemical type from the carboxylic anions.

Since the Brönsted relation holds equally well for a mixed deuterium water as for pure H_2O, a plot of log k_{D_2O} *versus* log k_{H_2O} should yield a straight line, provided log K_{D_2O} *versus* log K_{H_2O} exhibits the same linear relationship. That this conclusion is valid may be demonstrated as follows.

Figure 3 shows that the log k_{D_2O} points adhere closely to the linear equation

$$\log k_{D_2O} = x \log k_{H_2O} + C \qquad (5)$$

at both temperatures.

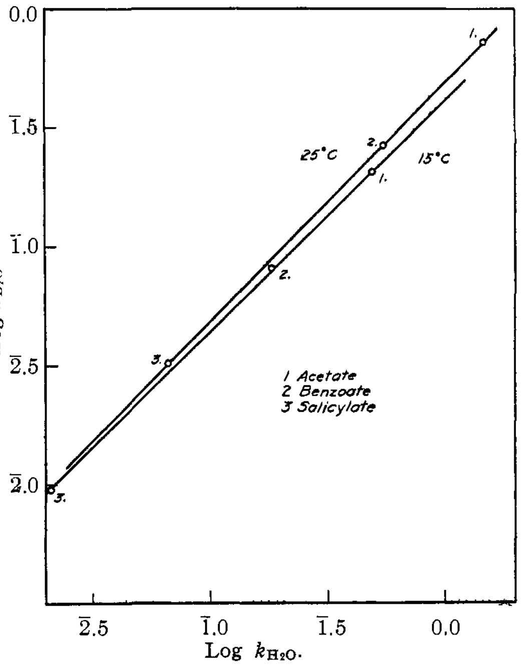

Fig. 3.—The logarithmic relation between the velocity constants in water and deuterium oxide at 15 and 25°: 1, acetate; 2, benzoate; 3, salicylate.

For light and heavy waters, respectively

$$\log k_{D_2O} = \log G_{D_2O} - \alpha' \log K_{D_2O} \qquad (6)$$

$$\log k_{H_2O} = \log G_{H_2O} - \alpha'' \log K_{H_2O} \qquad (7)$$

combining (5), (6) and (7) yields

$$\log K_{D_2O} = \frac{x\alpha''}{\alpha'} \log K_{H_2O} - \frac{x \log G_{H_2O} - \log G_{D_2O} + C}{\alpha'} \qquad (8a)$$

which is of the form

$$\log K_{D_2O} = y \log K_{H_2O} + C_0 \qquad (8b)$$

Substituting the kinetic data in equation (5): $x = 0.967$; $C = 9.611–10$ (Fig. 3); log $G_{H_2O} = 5.792–10$; log $G_{D_2O} = 4.998–10$; $\alpha' = 0.832$; $\alpha'' = 0.83$ (Table IV); yields $y = 0.965$ and $C_0 = -0.60$.

A plot of log K_{H_2O} *versus* log K_{D_2O} obtained from e. m. f.[13] data yields a straight line of slope $y = 0.972$ which is within 1% of the predictions, and $C_0 = -0.30$. The disagreement of 0.30 unit between the observed and calculated values of C_0 may arise from the uncertainty in executing the graphical solution, and in the accumulation of errors originally present in the constants obtained from equations (5), (6) and (7).

The studies of Brönsted and co-workers[14] on the decomposition of nitramide in *m*-cresol and H_2O furnish further data for testing this relation. Equation (4) holds in both solvents. The plot of the dissociation constants, log K_{cresol} *versus* log K_{H_2O} yield a linear relation with unit slope. In the case of velocities (Fig. 4) when the log k_{cresol} values of Brönsted, Nicholson and Del-

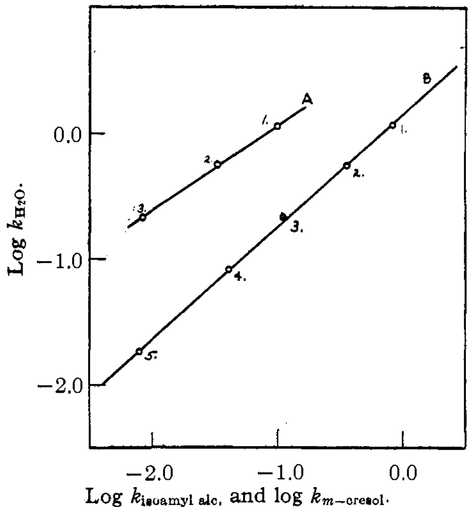

Fig. 4.—The logarithmic relation between the velocity constants in different solvents: A, H_2O *vs.* isoamyl alcohol; B, H_2O *vs.* *m*-cresol, 1, *p*-toluidine; 2, aniline; 3, *p*-chloroaniline; 4, *m*-chloroaniline; 5, *o*-chloroaniline.

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[12] Pedersen, *J. Phys. Chem.*, **38**, 581 (1934).

[13] Schwarzenbach, Epprecht and Erlenmeyer, *Helv. Chim. Acta*, **69**, 1292 (1936). Some of these data will require revision in the light of researches in progress in this Laboratory since the measurements involve galvanic cells with junction potentials. See Rule and La Mer, THIS JOURNAL, **60**, 1974 (1938).

[14] (a) Brönsted, Nicholson and Delbanco, *Z. physik. Chem.*, **169**, 379 (1934); (b) Brönsted, Delbanco and Tovberg-Jensen, *ibid.*, **169**, 361 (1934); (c) Brönsted and Duus, *ibid.*, **117**, 299 (1925); (d) Brönsted and Vance, *ibid.*, **A163**, 240 (1933).

banco are plotted against the log k_{H_2O} values of Brönsted and Duus, a straight line of slope x = 1.11 is also obtained. Since $\alpha_{H_2O} = 0.75$ and $\alpha_{m\text{-cresol}} = 0.84$, the calculated value for y in the equation corresponding to (8b) is $y = 0.99$, in excellent accord with the value of unity reported in reference (14b). A linear relation also obtains for the data of Brönsted and Vance[14d] using isoamyl alcohol as solvent (line A of Fig. 4).

Although several authors have shown that the logs of the dissociation constants in different solvents are related linearly when the solvents are as diverse as water, concentrated sulfuric acid and benzene,[15] no one appears to have called attention to the linear relationship between the logs of the velocity constants of a reaction obeying the Brönsted relation in two solvents.

The Arrhenius and Brönsted Equations.—Table IV summarizes the values of α and G in the Brönsted eq. (4). The decreases in rate arising either from a decrease in temperature or substitution of deuterium in the substrate and solvent are reflected almost exclusively in G and not in α. G may be interpreted as the rate for a hypothetical acid–base system K_A = unity. It appears that temperature and deuterium substitution operate primarily upon the fundamental kinetic properties of the substrate in the case of anion catalysis rather than upon the acid-base properties of the catalytic system.

TABLE IV

COMPARISON OF THE VALUES OF α AND G FROM THE BRÖNSTED EQUATION IN 91.5% D_2O WITH THOSE IN H_2O

Temperature, °C.		15	25
Present authors (D_2O)	α	0.83_2	0.84_5
	G	9.95×10^{-6}	2.94×10^{-5}
Baughan and Bell[11] (H_2O)	α	0.79_4	0.75_8
	G	8.44×10^{-5}	3.69×10^{-4}
Brönsted and Pedersen[16] (H_2O)	α	0.83	
	G	6.2×10^{-5}	

Baughan and Bell[11] report α equal to 0.76 at 25, 35 and 45°, but consider that the 4% increase to 0.79 at 15° is a real effect. Our data in D_2O do not support this view. Where comparisons can be made our data are in better agreement with those of Brönsted and Pedersen[16] than with those of Baughan and Bell.

In equation (3), $B = \log \frac{kT}{h} + \frac{\Delta S^*}{2.3R}$ where ΔS^* is Eyring's[17] entropy of activation which includes the contributions of all degrees of freedom (translational and internal) and kT/h is a pure frequency (ν) equal to $10^{14.6}$ (min.$^{-1}$) at 25°. In the collisional form of the statistical theory of kinetics,[18] kT/h is replaced by $Z°$, the collision frequency, which is equal to approximately $10^{12.2}$ (min.$^{-1}$) at 25°. In the notation of the English school, $B = \log A = \log PZ$; hence $\log P = S_{\text{act.}}/2.3R$. Here the entropy of activation, $S_{\text{act.}}$, as defined by La Mer,[18] does not contain the entropy contributions of the two translational degrees of freedom involved in the collision process. These contributions are contained in $Z°$.

Before the concept of entropy of activation was stressed[18] it was generally assumed that a catalyst effected an increase in rate solely by lowering the potential barrier (energy of activation). In Table V, we have decomposed $\Delta \log k = \Delta F^*/2.3RT$, where ΔF^* is the free energy of activation,

TABLE V

Catalyst referred to the "spontaneous" decomposition (H_2O) (11)	$\Delta \log k_{25}$	$\Delta \log A = \Delta B$	$-\Delta E/2.3RT$
Trimethylacetate	3.274	1.59	1.67
Acetate	3.082	1.97	1.10
Benzoate	2.652	1.61	1.04
Formate	2.318	1.33	0.96
Salicylate	1.735	1.28	.44
Monochloroacetate	1.579	1.01	.54
o-Nitrobenzoate	1.135	2.30	−1.20
Dichloroacetate	0.290	2.45	−2.19
Catalyst referred to the "spontaneous" decomposition (D_2O)			
Acetate	3.379	4.64	−1.28
Benzoate	2.939	2.99	−0.08
Salicylate	2.033	2.84	−0.83
Data in H_2O referred to D_2O for same catalyst			
Acetate	0.308	−1.55	1.85
Benzoate	.318	−0.26	0.59
Salicylate	.307	−0.44	.75
Spontaneous	.605	+1.12	− .52

R. P. Bell informs us (July 7, 1938) that the values in Baughan and Bell's Table IV[11] should be corrected to read

Monochloroacetic $A = 1.19 \times 10^{-13}$; E = 19,640
Dichloroacetic $A = 2.35 \times 10^{-14}$; E = 23,160

This produces a corresponding change in our Table V to read

	$\Delta \log k$	ΔB	$-\Delta E/2.3RT$
Monochloroacetate	1.574	0.80	0.77
Dichloroacetate	0.285	2.09	−1.81

These changes do not affect our conclusions.

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[15] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932); La Mer and Downes, *ibid.*, **55**, 1840 (1933); Hammett, *Chem. Rev.*, **13**, 61 (1933); La Mer, *ibid.*, **13**, 47 (1933).

[16] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[17] Eyring, *J. Chem. Phys.*, **3**, 107 (1935); Wynne-Jones and Eyring, *ibid.*, **3**, 494 (1935).

[18] La Mer, *ibid.*, **1**, 289 (1933).

into its component entropy and energy factors B and $E/2.3RT$, respectively. The data show that $\Delta \log k$, representing the catalytic effects of the anions referred to the solvent decomposition as a standard, is dominated more by an increase in the entropy of activation $\Delta B = \Delta S^*/2.3R$, than by a decrease in the energy of activation. This is particularly true of our data in 91.5% D. The only exception in H_2O is Baughan and Bell's result for trimethylacetate ion.

In their studies on the mutarotation of glucose, Hamill and La Mer[19] found that the increased catalysis of H^+ over that of the solvent decomposition, $\Delta \log k = 1.47$, was due to an increase in B of 3.48 units which was more than sufficient to overshadow the rate depressing effect of an increase of 1.95 units in $E/2.3RT$. Recently, Smith and Smith[20] report that the energy of activation of this reaction varies but very little with a series of catalysts. The marked changes in rate are due almost exclusively to a variation in $\log P$, *i. e.*, in the entropy of activation. From their data, B varies approximately as the square root of the acid dissociation constant K, a relation which Smith[21] had suggested previously for the acid–base catalyzed acetone–iodine reaction. The greater importance of entropy of activation is *not* confined to proton transfers but is illustrated also in the primary salt catalysis of ionic reactions. The Debye–Hückel limiting law requires that B increase with the square root of the ionic strength three times as rapidly as $E/2.3RT$.[22]

When the same anion catalyst operates in H_2O and in D_2O, we find (Table V) an almost constant difference in the free energy of activation ($\Delta RT \log k$), irrespective of the anion. The entropy and energy factors, however, appear to be specific to the anion, with the latter exercising a more predominant effect than the former.

Although equation (4) is a well-established empirical relation, which is obeyed closely in the nitramide decomposition and acetone–iodine reactions, no satisfactory theoretical derivation has been forthcoming. Brönsted[23] offered what he termed "a plausible (but) not absolutely cogent" development. Horiuti and Polanyi[24] "derive" equation (4) by assuming for a series of homologous reactions that

$$\log K = \Delta H/RT + \text{const.} \tag{9}$$

$$\log k = E/RT + \text{const.} \tag{10}$$

Equation (9) is an approximation which is not valid for the dissociation of weak acids over a range of temperature and does not hold for different acids since a change in the free energy of ionization between two acids is not generally followed by a corresponding change in the heat of ionization.[25] Horiuti and Polanyi's assumption that $\log k$ varies from catalyst to catalyst solely from changes in activation energy E is certainly not permissible in the light of the data discussed above. Any derivation which yields the Brönsted relation without consideration of entropy factors achieves the result by some fortunate cancellation which is not clear from the premises and the development.

Summary

1. Precision measurements of the anion catalysis of the decomposition of nitramide have been extended to waters of 91.5% deuterium content at 15 and 25°.

2. The velocity of anion catalysis is decreased approximately 2.3 fold at 15° and 2.0 fold at 25° for the bases, acetate, benzoate and salicylate ions on passing from H_2O to 91.5% D_2O.

3. The Brönsted equation $G = kK_A^\alpha$ relating velocity and dissociation constants holds accurately in D_2O. The exponent α characterizing the sensitivity of the substrate to basic catalysis is not perceptibly affected by temperature or by isotopic substitution. Most of the rate depressing effect of deuterium substitution is reflected in the constant G since K_A is also reduced.

4. Although the difference in the free energy of activation between proto and deutero forms is practically constant for these anion catalysts at 25°, the corresponding entropy and energy differences do not remain constant.

5. For a given solvent (H_2O) or (D_2O) the entropy factor is predominant in determining the rate for a series of anions, whereas for the same anion catalyst the energy of activation is the more important factor in deuterium substitution.

6. The spontaneous water reaction is of a different mechanism from the anion catalyzed process as judged by the influence of temperature and deuterium substitution.

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(19) Hamill and La Mer, *J. Chem. Phys.*, **4**, 395 (1936).

(20) Smith and Smith, *J. Chem. Soc.*, 1413 (1937).

(21) G. F. Smith, *ibid.*, 1744 (1934).

(22) La Mer and Kamner, THIS JOURNAL, **57**, 2662, 2668 (1935).

(23) Brönsted, *Chem. Rev.*, **5**, 231 (1928), pp. 318–321.

(24) Horiuti and Polanyi, *Acta Physicochimica, U. S. S. R.*, **2**, 505 (1935), pp. 516–520; Evans and Polanyi, *Trans. Faraday Soc.*, **34**, 23 (1938); see Guggenheim and Weiss' criticism, pp. 69–70 and the reply, p. 81.

(25) Hammett, *Trans. Faraday Soc.*, **34**, 73 (1938); *J. Chem. Phys.* **4**, 613 (1936).

7. The interdependence of the rates of a base catalyzed reaction and the dissociation constants of the catalysts on passing to new media is discussed in the light of the Brönsted equation. Attention is called to a linear relation between the logarithms of the rate constants in the two media.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Dissociation Constants of Deutero Acids by E. m. f. Measurements

BY C. K. RULE AND VICTOR K. LA MER

Although the dissociation constants of weak acids are decreased by a factor of two- to four-fold on passing from H_2O to D_2O, there is disagreement regarding the underlying theory. One school holds that the ratio of the dissociation constants of the proto and deutero forms of an acid is a function of the strength of the acid; the second that the ratio is constant for acids of a given type; a third,[1] that the ratio is uniformly three regardless of type.

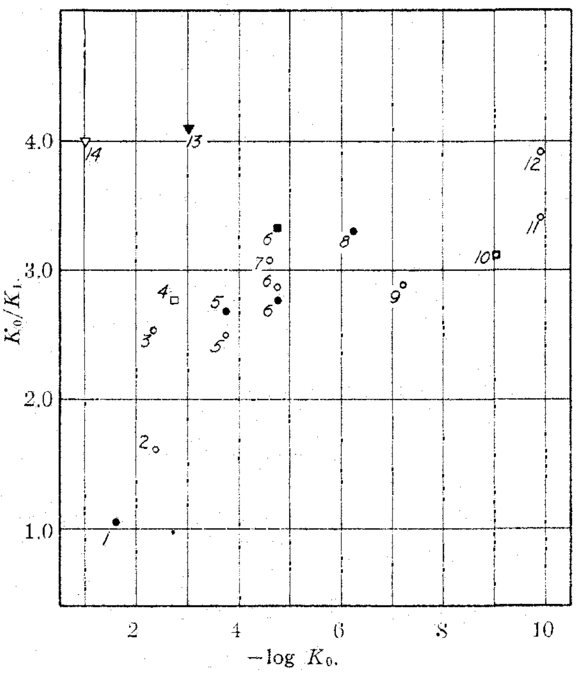

Fig. 1.—Dissociation constant ratios. Acids and references: 1 oxalic,[1a] 2 phosphoric (first),[3] 3 glycine,[3] 4 chloroacetic,[2] 5 formic,[1a,3] 6 acetic,[1a,4,23] 7 aniline hydrochloride,[3] 8 cacodylic,[1a] 9 phosphoric (second),[3] 10 ammonium chloride,[2] 11 glycine hydrochloride,[3] 12 trimethylamine hydrochloride,[3] 13 salicylic,[4] 14 picric.[1b] Methods of measurements: ● catalytic, ○ potentiometric with transference, □ conductimetric, ▽ distribution coefficient, ▼ potentiometric (approximate), ■ conductimetric and potentiometric without transference.

Lewis and Schutz[2] predicted that the ratio will depend on the strength of the acid—being larger the weaker the acid. They assumed that the potential field is unchanged by the substitution of a deuteron for a proton. Then the deutero acid will have a lower zero point energy and will be less dissociated, the difference increasing with decreasing strength of the acid. They mention that the difference in the extent of dissociation of the proto and deutero acids will depend also on the difference between their entropies of dissociation.

On the other hand, Schwarzenbach[3] concludes from measurements on cells with liquid–liquid junctions that the ratio is a function of the type of the acid, being smaller for carboxylic acids than for amine hydrochlorides.

A critical consideration of the data in the literature shows that there is little accurate work upon which to base a decision between these conflicting theories. These data are shown in Fig. 1. The ratios of the dissociation constants of the proto to those of the deutero acids are plotted against the logarithm of the dissociation constants of the proto acids. The differences of 15 and 20% between the ratios reported by different investigators for acetic acid are an indication of the inaccuracy of the data.

When accurate measurements are required, the uncertainty introduced by the presence of liquid–liquid junctions between H_2O and D_2O should be avoided in potentiometric studies. Korman and La Mer[4] have demonstrated the suitability of the quinhydrone electrode for measurements in H_2O–D_2O mixtures. We have accordingly reinvestigated their cells

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[1] (a) Hornel and Butler, *J. Chem. Soc.*, 1361 (1936); (b) Gross and Wischin, *Trans. Faraday Soc.*, **32**, 879 (1936); (c) Drucker, *Trans. Faraday Soc.*, **33**, 660 (1937).

[2] Lewis and Schutz, THIS JOURNAL, **56**, 1913 (1934). See also Halpern, *J. Chem. Phys.*, **3**, 456 (1935).

[3] Schwarzenbach, *Z. Elektrochem.*, **44**, 46 (1938).

[4] Korman and La Mer, THIS JOURNAL, **58**, 1396 (1936).