A mixture of 17 g. of ethyl propionate and 35 g. of phenyl benzoate was added to the ether solution of sodium triphenylmethyl at room temperature. After standing overnight the products were isolated in the usual manner. Only a little ethyl propionate and phenyl benzoate were recovered. Similar to the experiment with benzoyl chloride, the triphenylmethane was contaminated with high boiling oils. A small fraction (1.5 g.) boiling at 153–156° at 11 mm. which was apparently ethyl benzoylmethyl acetate was isolated.

A mixture of 17 g. of ethyl propionate and 26 g. of ethyl benzoate was added to the ether solution of sodium triphenylmethyl at room temperature. After fifteen minutes the mixture was acidified with acetic acid, and the products isolated in the usual manner. Some ethyl benzoate was recovered, and ethyl propionylmethylacetate was obtained. Four grams of ethyl benzoylmethylacetate boiling at 154–156° at 11 mm. was isolated. Hope and Perkin[15] give 162–163° as the boiling point at 18 mm. The isoxazolone melted at 120.5–121.5° (corr.). Haller and Bauer[16] give 123–124° as the melting point of the isoxazolone after many recrystallizations.

Summary

1. The enolate of ethyl isobutyrate has been condensed with benzoyl chloride, benzoic anhydride, and phenyl benzoate to give good yields of ethyl benzoyldimethylacetate.

2. Ethyl acetate in the presence of sodium triphenylmethyl gives a good yield of ethyl acetoacetate within three minutes.

3. Ethyl acetate and ethyl propionate condense with ethyl benzoate in the presence of sodium triphenylmethyl but only low yields of ethyl benzoylacetate and of ethyl benzoylmethylacetate have been obtained.

4. These reactions are regarded as examples of the Claisen type of condensation.

DURHAM, NORTH CAROLINA RECEIVED JUNE 11, 1938

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[15] Hope and Perkin, *J. chem. Soc.*, **95**, 2045 (1909).

[16] Haller and Bauer, *Ann. chim.*, [10] **1**, 282 (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Kinetics of the Hydrolysis of Ethyl Orthoformate in D_2O–H_2O Mixtures

BY FRANK BRESCIA AND VICTOR K. LA MER

Introduction

Recent work[1] on acid catalysis in heavy water has led to the general criterion that an increase in the rate in D_2O, over that in H_2O, is evidence that an equilibrium is maintained in the first stage of the reaction mechanism whereas a decrease in rate would indicate that the rate-determining step is a proton transfer in the first stage. In the case of a specific hydrogen-ion catalyzed reaction, the rate in H_2O–D_2O mixtures should be proportional to the relative concentration of D^+ and H^+, if these are the ionic species involved in the equilibrium. This was found to be the case for sucrose inversion,[2] which has been studied[3] over the range of H_2O–D_2O mixtures. We shall subject this hypothesis to further test by investigating the hydrolysis of ethyl orthoformate. This reaction,[4] which is specifically catalyzed by hydrogen ion, has been investigated carefully in H_2O for secondary salt[5] and solvent medium[6] effects. Recently, Hornel and Butler[7] have reported two measurements in a water of high deuterium content to determine the effect of deuterium substitution upon the dissociation constant of cacodylic acid.

Since the reaction is exceedingly sensitive to the concentration of hydrogen ions, acetic acid–sodium acetate buffers are well adapted for kinetic study. The thermodynamic and conductive properties of acetic acid have been studied carefully for the entire range of H_2O–D_2O mixtures.[8] The hydrolysis is accompanied by a relatively large volume change and therefore can be studied dilatometrically—a desirable characteristic when dilution must be avoided.

The velocity constant for a constant buffer ratio decreases steadily as the deuterium content of the solvent increases. This is contrary to the principle that the rate of a H^+ ion catalyzed reaction should increase. At the same time, however, the dissociation constant of acetic acid decreases 3.3-fold on passing from H_2O to D_2O so that it is possible that the rate when referred to the actual concentration of H^+ or D^+ ions increases.

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(1) Bonhoeffer, *Trans. Faraday Soc.*, **34**, 252 (1938); Wynne-Jones, *ibid.*, **34**, 245 (1938).

(2) La Mer, *Chem. Rev.*, **19**, 363 (1936); Hamill and La Mer, *J. Chem. Phys.*, **4**, 294 (1936).

(3) Moelwyn-Hughes and Bonhoeffer, *Naturwissenschaften*, **22**, 174 (1934); Gross, Suess and Steiner, *ibid.*, **22**, 662 (1934).

(4) Skrabal, *Z. Elektrochem.*, **33**, 322 (1927).

(5) Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

(6) Harned and Samaras, THIS JOURNAL, **54**, 1 (1932).

(7) Hornel and Butler, *J. Chem. Soc.*, 1361 (1936).

(8) Korman and La Mer, THIS JOURNAL, **58**, 1396 (1936); Chittum and La Mer, *ibid.*, **59**, 2425 (1937).

Experimental Procedure

1. **The Apparatus.**—To carry out measurements on limited quantities of heavy water, it was necessary to construct a semi-micro dilatometer (Fig. 1), whose capacity (10 cc.) is about 1/20 of the customary macro apparatus, by reducing the area of the capillary proportionately. The radius of the capillary bore is 0.1277 mm.; its uniformity, determined with a comparator, shows an average deviation of 0.3% the largest single deviation being 0.6%; it is sensitive to a volume change of 0.001% since a change of 0.02 cm. can be read easily (with experience readings can be made to ± 0.01 cm.). The expansion produced by 10 cc. of 0.05 *M* ethyl orthoformate is about 4 cu. mm., which corresponds to a change in height of about 8 cm.

The difficulty of leaking stopcocks was overcome effectively by the use of spring collars and mercury seals. Leakage was tested for by raising the mercury column in the capillary above that in the reaction chamber. The column remained constant at any fixed height over a period of time, long compared to the time needed to complete a run. No difficulty due to sticking was experienced; nevertheless a buzzer was attached at the top of the capillary. A lubricant was unnecessary. The entire dilatometer was immersed in a thermostat at 25.050 ± 0.002°, determined with a B. of S. calibrated platinum resistance thermometer.

2. **Materials.**—Merck C. P. acetic anhydride was redistilled and the middle fraction, 138–139°, collected.

Kahlbaum analytical grade sodium acetate was recrystallized below 80°, dried and pulverized. It was dehydrated between 45–50° for twelve hours and dried completely at 110° for twenty-four hours.

Eastman ethyl orthoformate was shaken several times in a separatory funnel with an aqueous sodium carbonate solution to decompose ethyl formate and neutralize formic acid. The ethyl orthoformate layer was separated, dried over calcium chloride, filtered and distilled. The fraction of b. p. 145–145.5° was retained.

H_2O–D_2O Mixtures.—Waters of 95–99% deuterium content from Norsk Hydro were treated as follows: (a) atmospheric pressure distillation from alkaline permanganate, (b) atmospheric pressure distillation from acid dichromate, (c) slow vacuum distillation. The reaction products, ethyl formate and ethyl alcohol, cannot be removed by distillation. The following technique proved satisfactory for the recovery of the solvent: (a) refluxed for about twelve hours with acid dichromate and distilled at atmospheric pressure; (b) refluxed with alkaline permanganate below the boiling point for twenty-four hours; (c) slow vacuum distillation. The chromate test for alcohol gives a negative result. The densities of the waters were determined in a 10-ml. pycnometer.

3. **Procedure.**—In the early experiments, the buffered solutions were prepared directly in a weight buret which may be connected to the dilatometer by a mercury-sealed glass ground joint. When larger quantities of deuterium oxide became available, 30 cc. of a reactant solution was prepared in a flask. Five cc. of acetic acid was freshly prepared for each experiment by adding acetic anhydride to the water. Several drops were then added to sodium acetate dissolved in water of the same D content. Fifteen cc. of the prepared buffer solution was pipetted into the dilatometer. When temperature equilibrium was established, 0.125 cc. of ethyl orthoformate was added and the mixture stirred with a motor. Suction was applied to the mercury reservoir and the solution followed into the reaction chamber; stopcocks were closed, suction turned off and the buzzer turned on. Readings were taken every two minutes. The elapsed time from the addition of reactant to first readings was about five minutes. The remaining portion of the solution, used within two days to check the first run, was kept in a refrigerator.

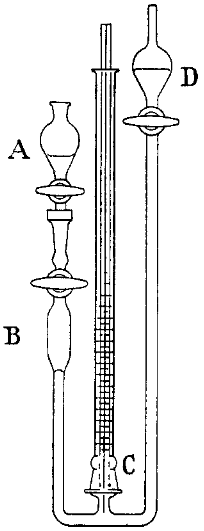

Fig. 1.—A, weight buret; B, reaction chamber; C, capillary; D, mercury reservoir. Approximately one-sixth actual size.

For a long period of time we were troubled with inability to obtain a constant end-point. The hydrolysis of ethyl orthoformate is complete within four hours, yet a very slow expansion of the solution continued over a period of two weeks. We first suspected hydrolysis of ethyl formate as a consecutive reaction. Investigation, however, established that this reaction produces no perceptible volume change. Dr. J. C. Hornel informs us that some previous investigators have corrected their end-point for drifts on the assumption that ethyl formate hydrolyzes slowly.

We observed that scrupulously cleaned apparatus yielded a satisfactory end-point but that on successive filling with duplicate solutions, the end-point reading continued to increase progressively with each refilling, until eventually refilling with water alone yielded a continuous slow expansion. We suspected bacterial decomposition. When the apparatus was sterilized with dilute nitric acid, washed with sterile water, and all buffer solutions preserved on ice, the difficulty entirely disappeared. With the technique described, we now achieve a final reading within six hours which remains constant to within ± 0.01 cm. for at least twenty-four hours.

The velocity constants were calculated by the usual first order formula

$$k = \frac{2.303}{t_2 - t_1} \log \frac{V_\infty - V_{t_1}}{V_\infty - V_{t_2}} \qquad (1)$$

where V_∞ and V_t are the dilatometer readings at time = ∞ and time = t; and also by Roeser's method of least squares for equal intervals.[9] The agreement between the two methods was always within 1%; the agreement between duplicate experiments was within 2%. A typical experiment is given in Table I, which shows the absence of drifts and freedom from sticking in the unusually narrow capillary.

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[9] Roeser, *Bur. Standards Bull.*, **16**, 363 (1920) (Scientific paper 388); Marlies and La Mer, THIS JOURNAL, **57**, 1812 (1935).

TABLE I

A TYPICAL EXPERIMENT

F_D = fraction of deuterium = $S(100)/0.1079$ = 25.91%. Molarity NaAc = 0.09732 mole/liter of solution. Molarity Ac_2O = 0.001010 mole/liter of solution.

	Run A				Run B	
t min.	V_t, cm.	t_1	t_2	k (eq. 1)	V_t, cm.	k (eq. 1)
0	8.84	0	14	0.0314	9.50	0.0314
2	9.40	2	16	.0317	10.10	.0314
4	9.95	4	18	.0320	10.64	.0312
6	10.47	6	20	.0318	11.18	.0314
8	10.95	8	22	.0320	11.67	.0313
10	11.40	10	24	.0320	12.11	.0315
12	11.85	12	26	.0317	12.56	.0315
14	12.23	0	24	.0316	12.98	.0313
16	12.62	0	26	.0316	13.36	.0313
18	12.99			Av. 0.0318	13.70	Av. 0.0314
20	13.31			a. d. 0.0002	14.06	a. d. 0.0001
22	13.63				14.37	
24	13.92				14.67	
26	14.20				14.96	
∞	18.40				19.30	

k by least square = 0.0317 = 0.0313

For comparison of the rate constants of different experiments, k is corrected to the rounded buffer ratio of 0.001000 M Ac_2O/0.1000 M NaAc.

$$\text{Thus } k_c = (0.0315)\,\frac{(0.09732)}{(0.001010)}\,\frac{(0.001)}{(0.1)} = 0.0304$$

The Specific Catalytic Coefficient of H_3O^+.—The specific catalytic coefficient $k_{H^+} = k/C_{H_3O^+}$. At a given ionic strength

$$C_{H_3O^+} = KC_{HAc}/C_{Ac^-}$$

$K = 2.87 \times 10^{-5}$ at $\mu = 0.1$ and 2.60×10^{-5} at $\mu = 0.05$, obtained by Harned and co-workers[10] in sodium chloride solutions, are used since the corresponding values for sodium acetate solutions are unknown.

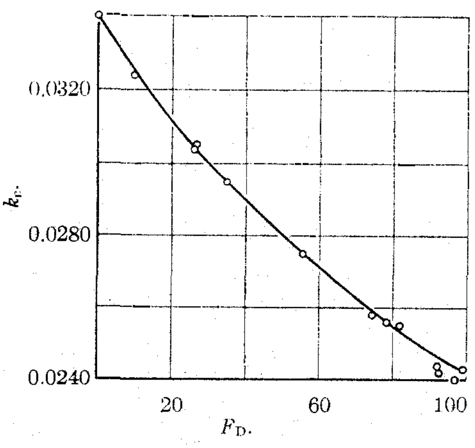

Fig. 2.

TABLE II

SPECIFIC CATALYTIC COEFFICENT OF H_3O^+

Molarity HAc	Molarity NaAc	Expts.	Av. k	$10^{-4}\,k_{H^+}$
0.0008918	0.08814	2	0.0171	6.02
.001422	.1434	1	.0185	6.03
.001312	.06573	2	.0311	5.81
.001989	.09941	2	.0336	5.85
.001926	.09616	2	.0341	5.98
.002255	.1128	2	.0348	5.92
.002444	.1214	1	.0358	5.95

Av. $k_{H^+} = 5.93 \times 10^4$; a. d. = 0.07

The average value $10^{-4}\,k_{H^+} = 5.93$ shown in Table II is in excellent agreement with the value of 6.0 reported by Harned and Samaras,[6] who employed a macro dilatometric method.

The experimental results for constant buffer ratio in mixtures of D_2O-H_2O are given in the first two columns of Table III, and are plotted against F_D in Fig. 2. The data exhibit the characteristic negative deviation from linearity.[11]

The specific catalytic coefficient of D_3O^+, k_{D^+}, is calculated from the value $k_C = 0.0242$ for $F_D = 100$, which is obtained by a short extrapolation from $F_D = 98$ in Fig. 2. C_{D^+} is obtained from

$$K_{DAc} = \frac{C_{D_3O^+} \cdot C_{Ac^-}}{C_{DAc}} = \frac{K_{HAc}}{3.3}$$

substituting 0.002 for C_{DAc}, 0.1 for C_{Ac^-}, and 2.87×10^{-5} for K_{HAc}. Hence, $k_{D^+} = 1.39 \times 10^6$ and the ratio of specific catalytic coefficients is

$$\frac{k_{D^+}}{k_{H^+}} = \frac{1.39 \times 10^6}{5.93 \times 10^4} = 2.35$$

This ratio is not in good agreement with the value 2.05 reported by Hornel and Butler.[7] Part of the discrepancy arises from the fact that these authors employed the value K_{HAc}/K_{DAc} 2.7_7 calculated from kinetic measurements. Our value 3.3 for the ratio of the dissociation constants is to be preferred since this value is obtained independently from e. m. f. and from conductance measurements.[8] Using 3.3, Hornel and Butler's k_{D^+}/k_{H^+} becomes 2.44, which is in better agreement.

Discussion

The concentration of protium and of deuterium ions in the mixtures of the oxides may be calculated from the kinetic data on the basis of the following considerations. The dissociation constants of acetic acid and of deuteroacetic acid are assumed to be independent of the deuterium content of the solvent water. This assumption is

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(10) Harned and Robinson, *ibid.*, **50**, 3157 (1928); Harned and Owen, *ibid.*, **52**, 5079 (1930).

(11) *Cf.* Refs. (2) and (4); La Mer and Greenspan, *Trans. Faraday Soc.*, **33**, 1266 (1937).

justified since the dielectric constants and the activity coefficients at constant ionic strength are practically independent of the D content of the solvent. That is

$$K_{\text{HAc}} = C_{\text{H}^+} C_{\text{Ac}^-} / C_{\text{HAc}} \qquad (2)$$

and is constant in any mixture of D_2O–H_2O at constant ionic strength. Similarly

$$K_{\text{DAc}} = C_{\text{D}^+} C_{\text{Ac}^-} / C_{\text{DAc}} \qquad (3)$$

in mixtures of D_2O–H_2O.

Twice the concentration of acetic anhydride equals the sum of the concentrations of acetic and deuteroacetic acids formed or

$$C_{\text{HAc}} + C_{\text{DAc}} = 2C_{\text{Ac}_2\text{O}} \qquad (4)$$

On the assumption that the velocity in D_2O–H_2O mixtures is proportional to C_{H^+} and C_{D^+}

$$k = k_{\text{H}^+} C_{\text{H}^+} + k_{\text{D}^+} C_{\text{D}^+} \qquad (5)$$

where k_{H^+} and k_{D^+} are the catalytic coefficients determined above and k, the measured rate constant in a water of deuterium content F_{D}.

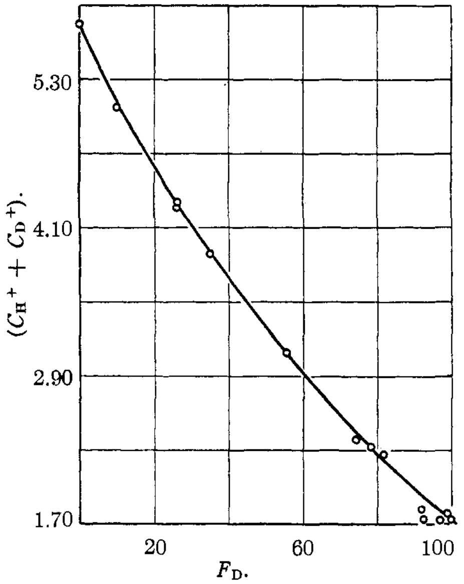

Fig. 3.

Dividing equation (2) by (3) and substituting C_{D^+} from (5), C_{DAc} from (4), and C_{HAc} from (2) gives

$$K = \frac{K_{\text{HAc}}}{K_{\text{DAc}}} = \frac{k_{\text{D}^+}}{k - k_{\text{H}^+} C_{\text{H}^+}} \left(\frac{2C_{\text{Ac}_2\text{O}} K_{\text{HAc}}}{C_{\text{Ac}^-}} - C_{\text{H}}{}^+ \right) \qquad (6)$$

from which

$$C_{\text{H}^+} = \frac{k_{\text{D}^+} 2C_{\text{Ac}_2\text{O}} K_{\text{HAc}}}{C_{\text{Ac}^-}(k_{\text{D}^+} - Kk_{\text{H}^+})} - \frac{Kk}{k_{\text{D}^+} - Kk_{\text{H}^+}} \qquad (7)$$

Hence, C_{H^+} can be calculated since all quantities on the right are known. k is the rate constant for buffer ratio 0.001 M Ac_2O/0.1 M NaAc denoted as k_c in Table III. Knowing the value of C_{H^+}, equation (5) yields C_{D^+}, and hence $(C_{\text{H}^+} + C_{\text{D}^+})$ and F_{D^+}, the fraction of deuterium ions. The sum $(C_{\text{H}^+} + C_{\text{D}^+})$ divided into k_c gives the specific catalytic coefficient, k_m, for each of the waters used, which is identical with k_{H^+} for H_2O and with k_{D^+} for D_2O.

A sample calculation of the typical experiment is given. Using equation (6)

$$3.3 = \frac{1.39 \times 10^5}{0.0304 - 5.93 \times 10^4 C_{\text{H}^+}} \left(\frac{2(0.001)(2.87 \times 10^{-5})}{0.01} - C_{\text{H}^+} \right)$$

and solving, $C_{\text{H}^+} = 3.62 \times 10^{-7}$. Solving equation (5)

$$0.0304 = (5.93 \times 10^4)(3.62 \times 10^{-7}) + (1.39 \times 10^5) C_{\text{D}^+}$$

$$C_{\text{D}^+} = 6.40 \times 10^{-8}$$

$$C_{\text{H}^+} + C_{\text{D}^+} = 4.26 \times 10^{-7}$$

$$F_{\text{D}^+} = \frac{0.64}{4.26} \times 100 = 15.02 \text{ and}$$

$$k_m = \frac{0.0304}{4.26 \times 10^{-7}} = 7.13 \times 10^4$$

The results of similar calculations are summarized in columns (3) to (7) in Table III.

TABLE III

(1) F_{D}	(2) k_c from expt.	(3) $C_{\text{H}^+} \times 10^7$ calcd. from eq. (6)	(4) $C_{\text{D}^+} \times 10^7$ calcd. from eq. (5) and column (3)	(5) $(C_{\text{H}^+} + C_{\text{D}^+})$ 10^7 from columns (3) and (4)	(6) F_{D^+} from columns (4) and (5)	(7) $k_m \cdot 10^{-4} = \frac{k_c}{C_{\text{H}^+} + C_{\text{D}^+}}$
0	0.0340	5.74	0.0	5.74	0	5.93
9.86	.0324	4.79	0.288	5.08	5.68	6.39
25.91	.0304	3.62	.640	4.26	15.0	7.13
26.40	.0305	3.68	.624	4.30	14.5	7.09
35.15	.0295	3.10	.799	3.90	20.5	7.57
55.60	.0275	1.93	1.16	3.09	37.5	8.90
74.51	.0258	0.944	1.45	2.39	60.6	10.8
78.49	.0256	.827	1.49	2.32	64.3	11.0
81.89	.0255	.769	1.50	2.27	66.1	11.2
91.88	.0244	.129	1.70	1.83	93.0	13.3
92.51	.0242	.01	1.73	1.74	99.4	13.9
96.95	.0240	.00	1.73	1.73	100	13.9
98.81	.0243	.07	1.72	1.79	96.1	13.6
100	(.0242)	0	1.74	1.74	100	13.9

The results are plotted in Figs. 3 and 4.

Figure 3 shows that $(C_{\text{H}^+} + C_{\text{D}^+})$ plotted against F_{D} gives a sagging curve similar to Fig. 2. k_m plotted against F_{D^+} (Fig. 4) gives a straight line in agreement with the results of the hydrogen ion catalyzed sucrose hydrolysis. This, however, is not a proof since in calculating the C_{D^+} we use equation (5) which is based on the assumption that the rate is proportional to F_{D^+}. But we do have sufficient data to check this assumption by calculating the dissociation constant, $K_{\text{H,D}}$, for a weak acid in H_2O–D_2O mixtures and comparing with values determined by La Mer and Chittum from conductance data. $K_{\text{H.D}}$ is de-

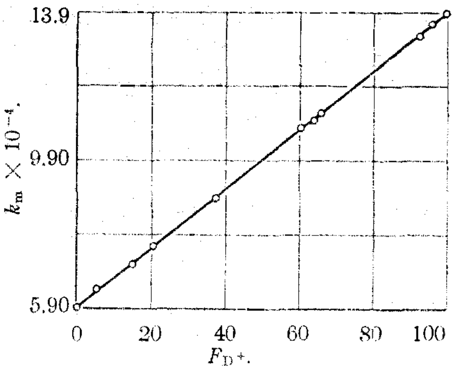

Fig. 4.

fined as $(C_{H^+} + C_{D^+})C_{Ac^-}/(C_{HAc} + C_{DAc})$. Substituting the values for $(C_{H^+} + C_{D^+})$, yields the results summarized in Table IV and plotted against F_D in Fig. 5. La Mer and Chittum's results[8] are represented by filled circles. Since the value 2.87×10^{-5} has been used for the dissociation constant of acetic acid for an ionic strength $\mu = 0.1$ and La Mer and Chittum report 1.84×10^{-5} for $\mu = 0$, we multiply their values by 1.56 for direct comparison. The kinetic results are in substantial agreement with those from conductance. This means that if we had not been able to calculate C_{H^+} and C_{D^+} from our kinetic data but were obliged to use the conductance data, the results would be substantially the same, *i. e.*, k_m plotted against F_{D^+} would yield a straight line, conforming to the basic assumption.

TABLE IV

F_D	$10^5 K_{H,D}$ Calcd. from kinetic data $\mu = 0.1$	$10^5 K_{H,D}$ La Mer and Chittum corr. to $\mu = 0.1$
0	2.87	(2.87)
9.86	2.54	
25.91	2.13	
26.40	2.15	
28.4		2.11
35.15	1.95	
48.4		1.70
55.60	1.55	
74.51	1.20	
77.1		1.16
78.49	1.16	
81.89	1.14	
91.88	0.92	
92.51	.87	
93		0.948
96.95	.87	
97		.897
98.81	.90	
100	.87	.87

The Rate-Determining Step.—The theory of intermediate complex formation offers two possibilities for the rate-determining step in an acid catalyzed reaction. The general scheme[12] may be represented as

$$\text{Substrate} + \text{HA} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{A}^- + (\text{Substrate, H}^+) \xrightarrow{k_3} \text{Products}$$

Adopting the usual assumption that in the stationary state the probability of disappearance of the complex is unity, the velocity of the reaction may be written as

$$V = -\frac{dC_S}{dt} = kC_SC_{HA} = \frac{k_1k_3}{k_2 + k_3} C_SC_{HA}$$

$$\text{or } k = k_1k_3/(k_2 + k_3)$$

Previous researches and discussions[13] have led to the general conclusion that the rate-determining step in a specific hydrogen-ion catalyzed reaction is the rate of decomposition of the complex (k_3), which when multiplied by the equilibrium constant of the reaction: reactants $\rightleftarrows$ complex, yields the rate of the reaction. Then, for the ratio of the rates in D_2O and in H_2O

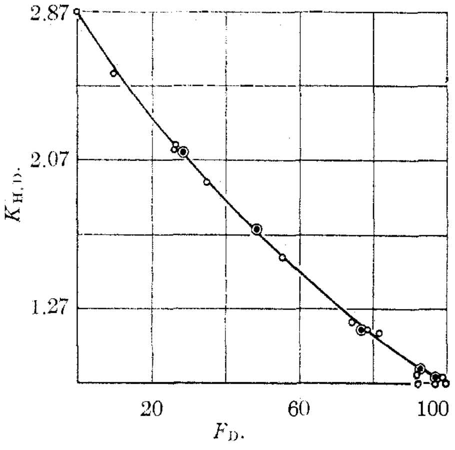

Fig. 5.—Results of La Mer and Chittum, ●.

$$\frac{k_{D^+}}{k_{H^+}} = \frac{k_{3SD^+}}{k_{3SH^+}} \frac{K_{SD^+}}{K_{SH^+}}$$

where K_{SD^+} and K_{SH^+} are the equilibrium constants involving the heavy and light complexes, respectively. From experiment, the ratio $k_{D^+}/k_{H^+} = 2.35$. If we assume the equilibrium in D_2O is shifted in favor of formation of SD^+ and if the rates of decomposition of SD^+ and SH^+ are

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(12) Skrabal, *Trans. Faraday Soc.*, **24**, 687 (1928).

(13) Pedersen, *J. Phys. Chem.*, **38**, 581 (1934); *Trans. Faraday Soc.*, **34**, 237 (1938); Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934); *Trans. Faraday Soc.*, **34**, 245 (1938); Bonhoeffer and Reitz, *Z. physik. Chem.*, **A179**, 135 (1937); Bonhoeffer, *Trans. Faraday Soc.*, **34**, 252 (1938); Reitz, *Z. Elektrochem.*, **43**, 659 (1937); *Naturwissenschaften*, **24**, 814 (1936); Wilson, *J. Chem. Soc.*, 1550 (1936); Bell, *Proc. Roy. Soc.* (London), **A154**, 414 (1936); ref. 7.

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_8O^+ 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

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[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

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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-

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[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).