

The Journal of the American Chemical Society

VOL. 54

JANUARY, 1932

No. 1

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

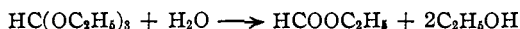
THE EFFECT OF CHANGE OF MEDIUM UPON THE VELOCITY OF HYDROLYSIS OF ETHYL ORTHOFORMATE¹

BY HERBERT S. HARNED AND NICHOLAS N. T. SAMARAS

RECEIVED JUNE 24, 1931

PUBLISHED JANUARY 7, 1932

The data on the influences of changes of media upon reaction velocities in homogeneous catalysis are fragmentary and to a large extent unreliable. As part of a general investigation of this subject, a careful study has been made of the velocity constant of hydrolysis of ethyl orthoformate catalyzed by acetic acid-sodium acetate buffers both in aqueous solution and in water-organic solvent mixtures. The hydrolysis of this reaction which may be represented by



was first studied quantitatively by Skrabal.² It is extremely sensitive to hydrogen ions and is therefore completed before any hydrolysis of ethyl formate is detectable. During the reaction no acid is formed and consequently this hydrolysis is admirably suited for the study of hydrogen-ion catalysis, particularly since hydroxyl ions produce no effect. Brönsted and Wynne-Jones³ showed that undissociated acid molecules show no detectable effect and that the hydronium ion is the effective catalyst.

Experimental Procedure

Materials.—All organic substances employed were the purest obtainable commercially. The ethyl orthoformate was procured from Kahlbaum and Schering and Kahlbaum, both samples yielding identical results. The glycine was a recrystallized sample of a highly pure product. The acetic acid and sodium acetate in the buffer mixtures were of the best grade of analyzed specimens. Small acid or basic impurities were compensated by the buffer, so that the concentration of the only active catalyst, the hydronium ion, was accurately controlled.

Apparatus.—The hydrolysis of ethyl orthoformate is accompanied by a considerable change of volume. The expansion of 100 cc. of a 0.05 *M* solution during the

¹ This paper contains part of a dissertation presented by Nicholas N. T. Samaras to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Skrabal, *Z. Elektrochem.*, **33**, 322 (1927).

³ Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

course of the reaction is about 40 cu. mm., so that the reaction velocity may be studied by the dilatometric method.

The dilatometer employed differed from that employed by Åkerlöf⁴ in not having a water jacket around the capillary. The capacity of the reaction vessel was about 125 cc. and the inner diameter of the capillary 0.7 mm.

With certain variations, the technique of operation was the same as described by Åkerlöf. Great care had to be exercised in filling the tubes, which in this case was accomplished more conveniently by pressure than by suction. Because of the sensitivity of the reaction, considerable precaution and acquired skill were necessary to attain the reported accuracy. The accuracy of determination of the velocity constant is estimated to be within $\pm 3\%$ in all cases, some of the series of results being considerably more accurate. The greatest difficulty in the dilatometric method is encountered when employing solvents more volatile than water.

Method of Calculation of Velocity Constants.—The reaction is of the first order and, consequently, the velocity constant, \bar{k} , may be computed by the equation

$$\bar{k}t = \log(v_{\infty} - v_0) - \log(v_{\infty} - v_t) \quad (1)$$

where v_{∞} , v_0 , v_t are the dilatometric readings corresponding to the final state, initial state and the state at the time t . All experimental values of \bar{k} will be given in common logarithms, according to equation (1), t being expressed in minutes. Owing to the uncertainty in the initial reading, \bar{k} was determined by plotting $\log(v_{\infty} - v_t)$ against t ; obviously, the negative of the slope is \bar{k} . All points were consistent and fell on a straight line with the possible exception of the first and second. This was caused by the fact that the solutions in passing over from the mixing flasks, which were immersed in the thermostat, to the reaction tubes were slightly cooled or heated due to small differences between the room temperature and that of the thermostat. Having chosen the value of v_0 , this graphical method was occasionally checked by an arithmetical calculation. The agreement was quite satisfactory.

Experimental Results

The catalytic coefficient of the hydronium ion was first determined at 20 and 25°. This measurement was carried out in order to check the value at 20° obtained by Brønsted and Wynne-Jones, who employed cacodylic acid-sodium cacodylate buffers as a source of hydronium ions. The velocity constant at both 20 and 25° was determined in a carefully prepared buffer solution containing 0.005 *N* acetic acid and 0.05 *N* sodium acetate. The velocity constant at 20°, \bar{k}_{20} , was found to be 0.0401, and at 25°, \bar{k}_{25} , 0.0641, respectively. These values represent the means of three experiments at each temperature. The temperature coefficient, $\bar{k}_{25}/\bar{k}_{20}$, equals 1.60.

To determine the catalytic coefficient it is essential to know the value of K_c of acetic acid at 25°, defined by the thermodynamic equation

$$K = \gamma_{\lambda}^2 \cdot K_c \quad (2)$$

⁴ Åkerlöf, THIS JOURNAL, 48, 3046 (1926).

in solutions containing sodium acetate. K is the dissociation constant of acetic acid, and γ_A , the activity coefficient of the acid, $\sqrt{\gamma_H \gamma_{AC} / \gamma_{HAC}}$. K_c in sodium acetate solutions is not known, so that we were obliged to use the values obtained by Harned and Robinson, and Harned and Owen⁵ in sodium chloride solutions. Their results give 1.75×10^{-5} , and 2.60×10^{-5} , and 2.87×10^{-5} at 0, 0.05, and 0.1 μ , respectively.

Since the oxonium ion is the only active catalyst, the catalytic coefficient, C' , may be readily obtained by dividing the velocity by the hydronium ion concentration. Since at a given ionic strength

$$K_c = \frac{m_{H_3O^+} m_{AC}}{m_{HAC}}, \text{ or } m_{H_3O^+} = K_c \frac{m_{HAC}}{m_{AC}} \quad (3)$$

we obtain for the catalytic coefficient at 20°

$$C_{20} = k/m_{H_3O^+} = 1.54 \times 10^4, \text{ and at } 25^\circ$$

$$C_{25} = C_{20} \times \frac{\bar{k}_{25}}{\bar{k}_{20}} = 2.46 \times 10^4$$

From the data of Brönsted and Wynne-Jones, C_{20} was found to be 1.49×10^4 , which we consider a good check since entirely different materials and a different form of dilatometer were employed by those investigators. By using 2.87×10^{-5} for K_c at $\mu = 0.1$, the values of C'_{25} given in Table I were obtained. Although the mean value at the higher ionic strength is somewhat greater than at 0.05 μ , we do not regard this as significant. The mean value of C'_{25} is 2.6×10^4 .

TABLE I
CATALYTIC COEFFICIENT AT 25°

Buffer	Detns.	\bar{k}	$C_{25} \times 10^{-4}$
0.005/0.05	3	0.0641	2.5
.001/0.1	2	.0080	2.8
.0111/0.1	1	.0870	2.7
.0098/0.1	2	.0744	2.6
.01/0.1	1	.0813	2.8
		Mean	2.6

The velocity constants in water and in water-organic solvent mixtures are given in Table II. Those in a given column were obtained by the same buffer mixture. As will be shown, the effect upon \bar{k} of change of medium is independent of small variations of hydronium ion concentration, and, therefore, the same buffer mixture was not employed for all experiments. The hydronium ion concentrations which are of the order of $10^{-6} M$ may always be obtained by dividing \bar{k} by the catalytic coefficient. Column (1) contains the concentration of organic solvent in moles per thousand grams of solution, column (2), the velocity constants, column

⁵ Harned and Robinson, THIS JOURNAL, 50, 3157 (1928); Harned and Owen, *ibid.*, 52, 5079 (1930).

(3), the values of $\log \bar{k}_0 - \log \bar{k}$, where \bar{k}_0 is the velocity in aqueous solution, and \bar{k} is the same in the water-solvent mixtures.

TABLE II
VELOCITY CONSTANTS OF HYDROLYSIS OF ETHYL ORTHOFORMATE IN WATER AND WATER-ORGANIC SOLVENT MIXTURES AT 25°

Catalyst: Acetic Acid-Sodium Acetate Buffers

I. Water-Methyl Alcohol Mixtures

c	\bar{k}	$\log \bar{k}_0 - \log \bar{k}$	c	\bar{k}	$\log \bar{k}_0 - \log \bar{k}$
0.0	0.0440	0.0	0.0	0.0263	0.0
.1	.0437	.0030	.779	.0240	.0397
.3	.0424	.0161	1.51	.0216	.0855
.5	.0413	.0275	2.20	.0195	.1299
.7	.0407	.0339	2.85	.0183	.1575
3.0	.0300	.1663	3.60	.0160	.2158

II. Water-Ethyl Alcohol Mixtures

0.0	0.0287	0.0	0.0	0.0253	0.0
.536	.0258	.0463	1.05	.0209	.0830
1.05	.0234	.0867	2.78	.0144	.2448
1.56	.0208	.1398			
2.45	.0177	.2099			
3.32	.0142	.3050			

III. Water-*n*-Propyl Alcohol Mixtures

0.0	0.0263	0.0			
.421	.0235	.0489			
1.20	.0187	.1481			
1.27	.0183	.1575			
1.91	.0151	.2410			
2.25	.0136	.2864			

IV. Water-*n*-Butyl Alcohol Mixtures

0.0	0.0410	0.0			
.342	.0359	.0577			
.660 ^a	.0316	.1131			

^a Limited solubility in water.

V. Water-Isopropyl Alcohol Mixtures

0.0	0.0388	0.0	0.0	0.0263	0.0
.412	.0343	.0535	1.18	.0186	.1504
.797	.0308	.1003	1.88	.0156	.2268
1.16	.0290	.1264	2.20	.0145	.2586
1.50	.0260	.1739			
1.78	.0240	.2086			

VI. Water-Acetone Mixtures

0.0	0.0253	0.0			
.430	.0229	.0433			
.837	.0212	.0768			
1.23	.0185	.1359			
2.05	.0153	.2184			

TABLE II (Concluded)

VII. Water-Glycerin Mixtures

c	\bar{k}	$\log \bar{k}_0 - \log \bar{k}$	c	\bar{k}	$\log \bar{k}_0 - \log \bar{k}$
0.0	0.0298	0.0			
.571	.0292	.0088			
1.58	.0268	.0461			
1.60	.0268	.0461			
2.09	.0267	.0477			
2.33	.0260	.0592			

VIII. Water-Glycine Mixtures

0.0	0.0500	0.0
.3	.0550	-.0414
.5	.0571	-.0577
1.0	.0590	-.0719

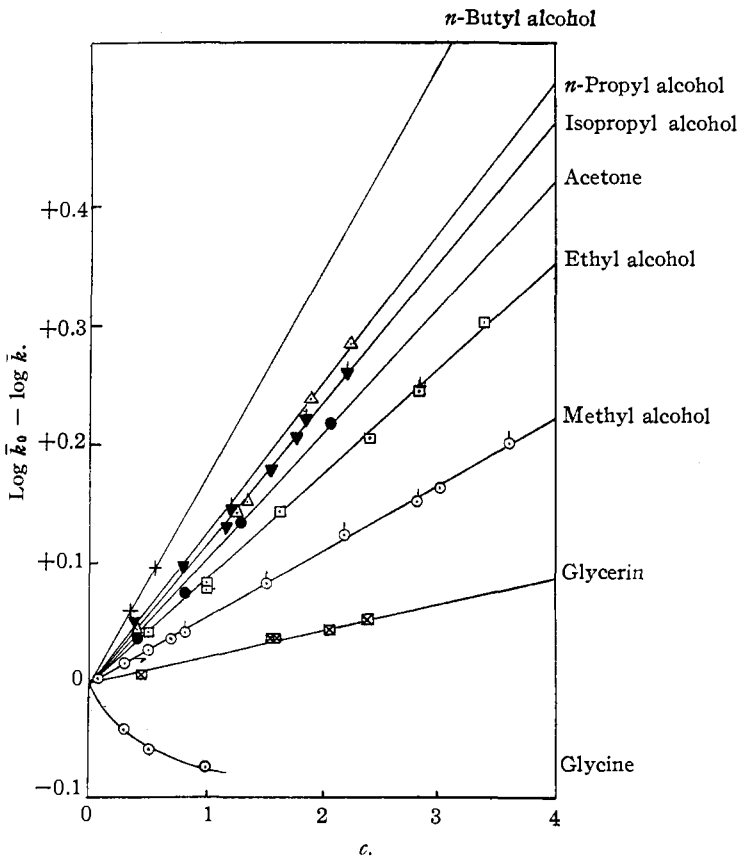


Fig. 1.—Plots of $\log \bar{k}_0 - \log \bar{k}$ against c .

Discussion of Results

In Fig. 1, the values of $\log \bar{k}_0 - \log \bar{k}$ have been plotted against c , the concentration in moles of organic solvent per thousand grams of solution. Except in the case of glycine, all these curves are straight lines. Further, the slopes are independent of the strength of the buffer, as shown by the superposition of the plots of the two series of results in the cases of the water-methyl, -ethyl and -isopropyl alcohol mixtures.

Let us now compare those results with the lowering of the dielectric constant of water by the addition of the compounds in question. Unfortunately, with the exception of water-methyl alcohol, water-acetone, water-glycine mixtures, complete data are not available. On the other hand, the dielectric constants of all the pure substances with the exception of glycine are known. The dielectric constants of the water-methyl alcohol, and water-acetone mixtures are given in Table III.⁶

TABLE III
DIELECTRIC CONSTANTS OF SOLVENTS

I. Mixtures					
Frequency of applied e. m. f., 4×10^8					
(1) Water-Methyl Alcohol Mixtures, $t = 17^\circ\text{C.}$			(2) Water-Acetone Mixtures, $t = 19^\circ\text{C.}$		
Alcohol, % by wt.	D	$D_1 - D$	Alcohol, % by wt.	D	$D_1 - D$
0.0	82.6	0.0	0.0	81.8	0.0
10	77.6	5.0	25	67.7	14.1
20	72.8	9.8	50	51.2	30.6
40	63.0	19.6	80	32.2	49.6
60	52.0	30.6	100	20.7	61.1
80	42.6	40.0			
100	33.8	48.8			

II. Compounds		
Substance	$t, ^\circ\text{C.}$	$D(\nu = 4 \times 10^8)$
Water	20	81.9
Methyl alcohol	20	33.1
Ethyl alcohol	20	22.0
Acetone	19	20.7
Isopropyl alcohol	20	15.7
<i>n</i> -Propyl alcohol	20	12.3
<i>n</i> -Butyl alcohol	19	7.8
Glycerin	20	{ 16.5 43.0 ($\nu = 7.5 \times 10^8$)

In Fig. 2, $D_I - D$ has been plotted against weight percentage of methyl alcohol and acetone. The results yield straight lines throughout the entire range of concentration. In the absence of any data concerning the dielec-

⁶ "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. VI, p. 81.

tric constants of the other mixtures, we shall assume that the same linear relation maintains. In Table III, Part II, are given the values for the dielectric constants of the pure substances from the "International Critical Tables." If the linear relation holds, the curves in Fig. 2 represent the distribution of the results. The plot of $D_1 - D$ against weight per cent. of glycine, which is also given, is not a straight line. With the exception of glycerin, the order of the results is the same as that of the $\log \bar{k}_0 - \log \bar{k}$ against C plots in Fig. 1. However, if we use the value for the dielectric constant of glycerin at $\nu = 7.5 \times 10^5$, the result is reasonable.

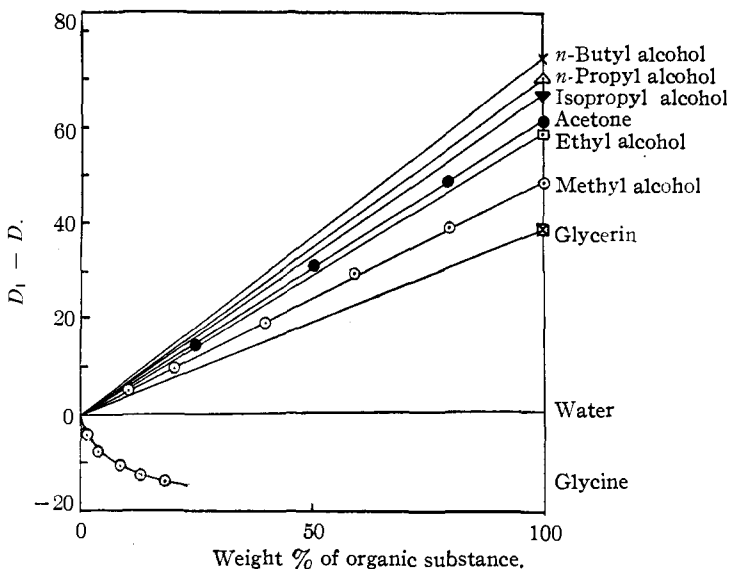


Fig. 2.—Plots of $D_1 - D$ against wt. % of organic substance.

From these results, we find that

$$\log \bar{k}_0 - \log \bar{k} = aC \quad (4)$$

and

$$D_1 - D = bC \quad (5)$$

which upon combination give

$$\log \bar{k}_0 - \log \bar{k} = \frac{a}{b} (D_1 - D) \quad (6)$$

In Table IV are given the experimental slopes, a and b , and their ratio.

The constancy of the values in the last column of Table IV shows quite definitely the dependence of the velocity constant upon the dielectric constant. If we plot $(\ln \bar{k}_0 - \ln \bar{k})$ against $(D_1 - D)$, a single straight line is obtained, with a slope equal to 2.3×0.032 , or 0.07. Therefore

$$\ln \bar{k}_0 - \ln \bar{k} = 0.07 (D_1 - D) \quad (7)$$

TABLE IV
 a AND b VALUES OF EQUATIONS 4 AND 5

	a	bb	a/b
Methyl alcohol	0.0565 ^a	1.564	0.036
Ethyl alcohol	.090 ^a	2.759	.033
Acetone	.105	3.553	.030
Isopropyl alcohol	.118 ^a	3.977	.030
<i>n</i> -Propyl alcohol	.128	4.182	.031
<i>n</i> -Butyl alcohol	.171	5.491	.031

Average 0.032

^a Average of two series. ^b The values of b have been computed from $b = (D_W - D_A)/1000 \times W$, where W is the molecular weight of the solvent, and D_W and D_A are the dielectric constants of water and organic solvent, respectively. The dielectric constants are at 20° while the velocity constants were determined at 25°. No temperature correction has been applied since the data are very scarce. This omission will not affect the relative lowering very much; indeed, the correction would not be any greater than the uncertainty of the D -values.

Further, the case of water-glycine solutions is interesting. $D_I - D$ for glycine is negative and the plot of $(D_I - D)$ against weight per cent. is of the same form as the corresponding velocity curve in Fig. 1. In addition $(\ln \bar{k}_0 - \ln \bar{k})/(D_I - D)$ is nearly constant but the slope is only 0.015 instead of 0.07.

Summary

1. The hydrolysis of ethyl orthoformate, a reaction characterized by constancy of the solution acidity, has been investigated experimentally by employing acetic acid-sodium acetate buffers. A dilatometric procedure similar to that described by Åkerlöf has been followed. The catalytic coefficient of the hydronium ion, the only active catalyst in this reaction, has been determined; the result is in good agreement with that obtained by Brønsted and Wynne-Jones, who made use of cacodylic acid-sodium cacodylate buffers.

2. The variations of the velocity constant in water mixtures of methyl, ethyl, *n*-propyl, isopropyl and *n*-butyl alcohols, acetone, glycerin and glycine have been obtained. With the exception of the glycine solutions, all the other series of measurements led to the following single equation for the dependence of the velocity constant lowering upon the dielectric constant lowering

$$\ln \bar{k}_0 - \ln \bar{k} = 0.07 (D_1 - D)$$

In the case of glycine there is an increase in both $\ln \bar{k}$ and D , neither, however, varying linearly with the glycine concentration, although $(\ln \bar{k}_0 - \ln \bar{k})/(D_I - D)$ is practically constant and equal to 0.015.

3. A theoretical treatment of those results, as well as other medium changes in homogeneous catalysis, is given in the paper following.