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CATALYSIS IN THE HYDRATION OF ACETIC ANHYDRIDE[1]

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In a general paper on reaction velocity, Skrabal[2] has regarded the hydrolysis of the organic oxides as made up of (*a*) a hydrogen-ion catalyzed reaction, (*b*) a hydroxyl-ion catalyzed reaction, (*c*) an uncatalyzed or water reaction. This classification was first made by Hudson, who applied it to the case of the mutarotation of glucose. Brönsted and Guggenheim[3] studied the effect on the mutarotation of glucose of other acid molecules than hydrogen ion, and of other basic molecules than hydroxyl ion; they showed that water may be considered to act catalytically both as an acid and as a base. Similarly, in the decomposition of nitramide, water may be classed as a basic catalyst,[4] since the constant for the decomposition of nitramide in acidified water lies on the straight line obtained when one plots the logarithm of the basic catalytic constant against the logarithm of the constant of basic strength. In all cases where catalytic effects of other acid molecules than hydrogen ion and other basic molecules than hydroxyl ion have been detectable, a water reaction has also been found to occur.[5] Conversely, it should be interesting to investigate from the point of view of acid and basic catalysis, a substance showing a particularly fast water reaction relative to the hydrogen- and hydroxyl-ion catalyzed reactions.

Acetic anhydride is such a substance. As Skrabal points out, the accurate determination of the catalytic effects of hydrogen and hydroxyl ion has not been possible because the minimum reaction rate already lies close to the limit of measurability. Skrabal[6] followed the hydration of acetic anhydride by coupling it with the iodide–iodate reaction; he assigns to the constant of hydroxyl ion catalysis the value $k_{\mathrm{OH}^-} \leqq 4.4 \times 10^6$ at 25°. More recently Szabó[7] has studied the hydration of acetic and succinic anhydrides at 14 and 18° in the presence of electrolytes and non-electrolytes, using an interferometer to measure the change in refractive index which accompanies the reaction. Szabó reports catalysis by hydrogen

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[1] In memory of Ira Remsen.

[2] Skrabal, *Z. Electrochem.*, **33**, 322 (1927).

[3] Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

[4] Brönsted and Pedersen, *Z. physik. Chem.*, **113**, 389 (1924).

[5] In the case of the acetone–iodine reaction, a water reaction has not been detected experimentally, but it has been inferred from calculations (Dawson and Key, *J. Chem. Soc.*, **1928**, p. 543).

[6] Skrabal, *Monatsh.*, **43**, 493 (1922).

[7] Szabó, *Z. physik. Chem.*, 122, 405 (1926).

and acetate ions in the case of acetic anhydride and by hydrogen and succinate ions in the case of succinic anhydride. Practically all her experiments, however, were carried out in solutions of high electrolyte concentration and no proportionality between catalyst concentration and reaction rate is shown. Orton and Jones[8] studied the reaction in acetic acid, in acetic anhydride, in acetone, and in various mixtures of these solvents with water. From their experiments with different acids, they conclude that the non-ionized acids are effective catalysts in a solvent of over 90% acetic acid. They also notice the catalytic effect of sodium acetate in aqueous solutions but do not distinguish it from the effect of hydroxyl ion. The reaction has also been studied by Verkade,[9] who measured the change in the conductivity, and by Benrath,[10] who determined the change in the density of the solution as the reaction proceeded.[11]

It was thought that a dilatometric method might be convenient. Preliminary experiments showed that there was a considerable heat of reaction, a fact which appears often to have been overlooked and which is of the utmost importance in dilatometric work. A dilatometer was designed to take care of the heat of reaction and experiments were carried out at 0°. Here the half time of the reaction is twenty-six minutes. It was found possible to measure accurately the rate of reaction where the half time is as little as ten minutes.

Experimental Method

The apparatus as shown in Fig. 1 consists of a mixing chamber A connected by means of capillary tubing through the stopcock E to the two arms of the dilatometer F,F′ and so to the calibrated capillary G. F and F′ have a capacity of approximately 25 cc. each and the bore of the capillary G is 0.4 mm. In addition, the mercury filled chamber, J, is connected at D. A steel cap is sealed into the chamber J and the steel screw H turning through this cap acts as a plunger. By turning the screw the mercury can be raised through D and through E to K and K′. The whole apparatus is mounted and set in the Dewar P. Since the apparatus is packed in ice, and since it is necessary to observe the mercury levels at D and N, the tubes M and N extending to the walls of the Dewar are affixed with suitable supports. The stopcock E is encased; in addition it is fitted with a spring to hold the cock tightly in the barrel and with a mechanical arrangement for turning the cock.

A description of the procedure will further explain the apparatus. The glass rod B with a ground tip is set in place and 50 cc. of the solution run into the chamber A. A is then closed by a rubber stopper. The apparatus is packed tightly in snow ice and sufficient ice water added to fill the Dewar. After an hour a platinum stirrer and thermometer are placed in A. The stopcock E is opened and the level of the mercury adjusted to D by means of the screw H; this could be observed through M. When the solution has come to 0.0° ± 0.01°, the thermometer is removed and 0.35 cc.

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[8] Orton and Jones, *J. Chem. Soc.*, 101, 1708 (1912).

[9] Verkade, *Rec. trav. chim.*, **35**, 79, 299 (1915).

[10] Benrath, *Z. physik. Chem.*, *67*, 501 (1909).

[11] A more complete list of references is given by Verkade (ref. 9) and Skrabal (ref. 6).

of acetic anhydride is added from a small weight pipet. After mixing, the rod B is removed and a rubber stopper with glass tube inserted in the top of the mixing chamber. The tube is connected to a suitable pressure system and the solution is forced over through the cotton plug C into the dilatometer and up into the capillary G. The rubber stopper is then removed from A and the rod B replaced. By turning H mercury is forced up to K and K′. Any excess of solution is taken up with filter paper and by turning H the liquid is brought to a suitable level in the capillary, E is closed and B removed. The rubber stopper is replaced in A, the Dewar wrapped in an insulating jacket and at a convenient time the first reading is taken. The manipulation occupies from six to ten minutes from the time of mixing. If, as occasionally happens, an air bubble is trapped between D and E it appears on the surface of the mercury when the mercury is forced up to N and is easily seen. It is a simple matter to draw the mercury back, remove B, and after inserting a rubber stopper in the top of L remove the bubble by gentle suction at R. Very little trouble was experienced with air bubbles; on the whole the method of filling a dilatometer by pressure is superior to filling by suction.

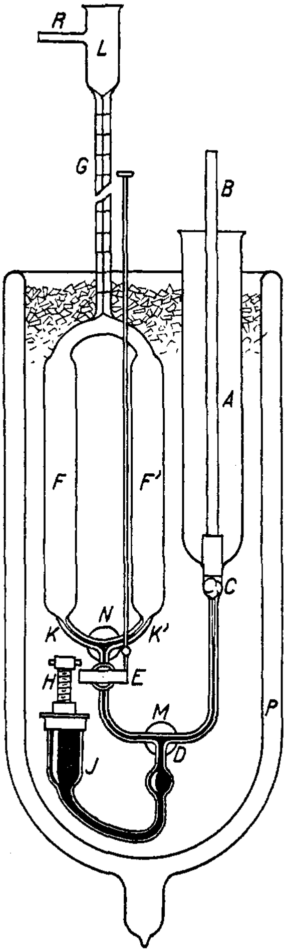

Fig. 1.—Apparatus.

Readings were taken at minute intervals for thirty minutes and at two minute intervals for another thirty minutes. One-half hour later a second set of readings was made, at the same intervals, and the velocity constant was calculated by the method of Guggenheim.[12] In those cases where the infinity reading was observed, the velocity constant was also calculated from the usual monomolecular formula. The observed infinity reading and that calculated from the velocity constant of Guggenheim's method usually agreed within 0.05 cm. for a total contraction of 6 cm. in the capillary. Since it is difficult to reproduce briefly an experiment calculated by the plotting method, Table I gives, for a typical experiment, the constant obtained from the observed infinity value and the formula $k = 1/t \ln (V_0 - V_\infty)/(Vt - V_\infty)$.

In no case was there a trend of more than 2% in the value of k during the course of an experiment. The change in k[13] with change in concentration of anhydride was not investigated, the initial concentration being 0.07 M ± 10% in all cases. The medium effect of acetic acid was investigated and will be discussed later. The anhydride used was a fraction of Kahlbaum's "für analytische

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

[13] Rivett and Sidgwick, *J. Chem. Soc.*, **97**, 732 (1910).

TABLE I

EXPERIMENT IN DISTILLED WATER

First reading after ten minutes. (Anhydride) = 0.07 M, T = 0° C.

Time, min.	Dilatometer reading	$V-V_\infty$	log $V-V_\infty$	0.434 k min.$^{-1}$	Time, min.	Dilatometer reading	$V-V_\infty$	log $V-V_\infty$	0.434 k min.$^{-1}$
0	18.27	5.99	0.777	....	25	15.34	3.06	0.486	0.0117
1	18.10	5.82	.765	0.0120	26	15.27	2.99	.476	.0116
2	17.94	5.66	.753	.0120	27	15.19	2.91	.464	.0116
3	17.80	5.52	.742	.0117	28	15.10	2.82	.450	.0117
4	17.66	5.38	.731	.0115	29	15.02	2.74	.438	.0117
5	17.50	5.22	.718	.0118	30	14.96	2.68	.428	.0118
6	17.37	5.09	.707	.0117	32	14.82	2.54	.405	.0116
7	17.23	4.95	.695	.0117	34	14.68	2.40	.380	.0117
8	17.10	4.82	.683	.0118	36	14.55	2.27	.356	.0116
9	16.99	4.71	.673	.0116	38	14.41	2.13	.328	.0118
10	16.87	4.59	.662	.0115	40	14.30	2.02	.305	.0118
11	16.74	4.46	.649	.0116	42	14.20	1.92	.283	.0118
12	16.62	4.34	.637	.0117	44	14.09	1.81	.258	.0118
13	16.51	4.23	.626	.0117	46	13.98	1.70	.230	.0119
14	16.40	4.12	.615	.0116	48	13.91	1.61	.207	.0119
15	16.29	4.01	.603	.0116	50	13.80	1.52	.182	.0119
16	16.19	3.91	.592	.0116	52	13.73	1.45	.161	.0118
17	16.09	3.81	.581	.0116	54	13.65	1.37	.137	.0119
18	15.99	3.71	.569	.0116	56	13.57	1.29	.111	.0118
19	15.89	3.61	.557	.0116					
20	15.79	3.51	.545	.0116	∞	12.28			0.0117
21	15.70	3.42	.534	.0116	∞ calcd.	12.26			k = 0.0269
22	15.60	3.32	.521	.0116					
23	15.51	3.23	.509	.0117					
24	15.42	3.14	.497	.0117					

The constant[a] calculated by Guggenheim's method is 0.434 k min.$^{-1}$ = 0.0118 or k = 0.0271.

[a] All the remaining constants in this paper are given in terms of natural logarithms.

Zwecke" distilling between 137 and 138° at 753 mm. Other samples of anhydride gave constants not differing by more than 2% from 0.0269.[14]

On account of the high constant of the spontaneous or water reaction, the effects of H_3O^+ and OH^- ions are practically negligible over a wide range. Taking[15] k_{OH^-} as 4×10^5, $k_{H_3O^+}$ as 3×10^{-2} and k_0 as 3×10^{-2} at 0°, for a hydroxyl-ion concentration of 1×10^{-8} M, the effect of hydroxyl ion is only 1% of the total reaction and for a hydrogen-ion concentration of 1×10^{-2} M the effect of the hydrogen ion is 1% of the whole. As will be shown later, k_{Ac^-} is of the same order of magnitude as $k_{H_3O^+}$; any catalysis by the acetate is therefore negligible in the experiments carried out to determine k_0.

Table II shows the influence on k_0 of small amounts of hydrochloric acid and of neutral salts present in concentrations up to 0.2 N.

The salt effect is negative and varies with the individual salt. The

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[14] Szabó, ref. 7, p. 411.

[15] k_0 is used for the water reaction in distinction from k_{H_2O} which is $k_0/55$.

Table II

Effect of Neutral Salts

Acid-salt	Acid, moles per liter	Salt, moles per liter	Velocity constant, k_0
HCl	0.002–		0.0269[a]
	.0004	0	.0267
HCl–NaCl	.0008	0.059	.0263
HCl–NaCl	.001	.099	.0262
HCl–NaCl	.0008	.138	.0260
HCl–NaCl	.0008	.198	.0258
HCl–NaCl	.002	.198	.0255
HCl–KCl	.0008	.198	.0253
HCl–KCl	.0008	.198	.0250
HNO_3–KNO_3	.0008	.198	
HNO_3–KNO_3	0.0008	0.099	0.0261
CCl_3COOH–CCl_3COONa	.0008	.198	.0260
HCl–NH_4Cl	.0008	.198	.0259
$HClO_4$–$NaClO_4$	.0015	.087	.0261
$HClO_4$–$NaClO_4$	.0015	.174	.0251
$HO_3SC_6H_5$–$NaO_3SC_6H_5$	.0015	.079	.0254
$HO_3SC_6H_5$–$NaO_3SC_6H_5$	.0015	.0108	.0248

[a] Average values.

results for sodium chloride are plotted in Fig. 2; these results can also be expressed by the equation $k_0 = 0.0269 - 0.0052\,c$ (where c is the concentration of sodium chloride).

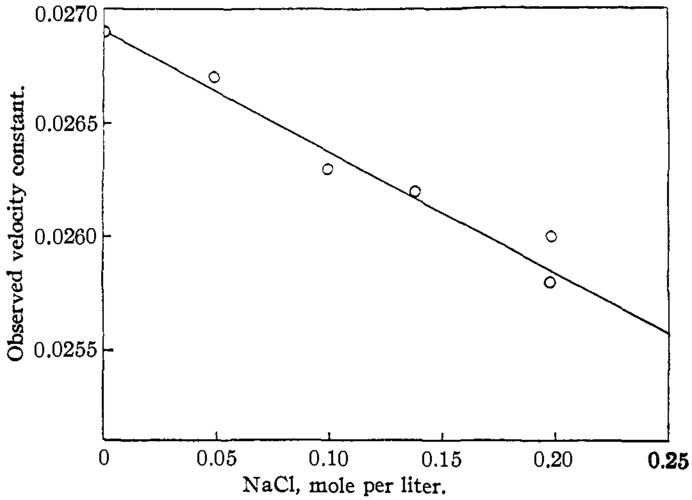
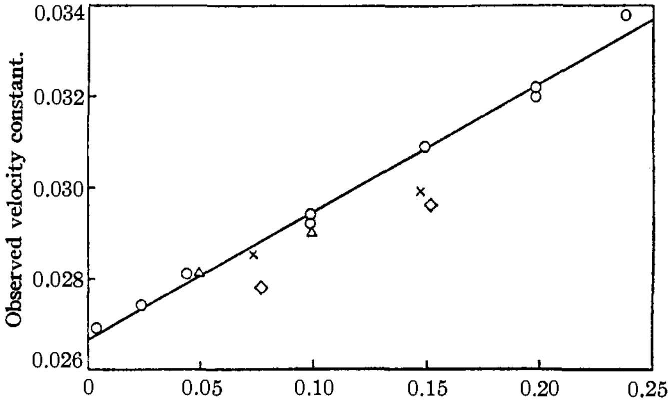


Fig. 2.—Effect of sodium chloride on reaction rate.

Figure 3 and Table III give the results of experiments carried out to determine $K_{H_3O^+}$. In Fig. 3 the observed velocity constants are plotted against the acid concentrations.

The plot shows approximate proportionality between acid concentration and increase in velocity constant; however, the correction for salt effect on the velocity constant remains to be made. In Table III the correction is made and $K_{H_3O^+}$ is computed.

The third column of Table III gives the observed velocity constant. The fourth gives k_0 corrected for salt effect, the effect for each acid being taken equal to the value shown in Table II for the corresponding salt. In the case of hydrochloric acid the effect is taken to be the same as that of sodium chloride. Col. 5 shows the portion of the reaction due to the hydrogen ion and $K_{H_3O^+}$ (sixth column) is obtained by dividing $k_{obs.} - k_0$ by the acid concentration. When it is considered that an error of 1%



⊙, HCl; △, HNO_3; × $HClO_4$; ◇, $HO_3SC_6H_5$.

Fig. 3.—Effect of hydrogen ion on reaction rate.

TABLE III

EFFECT OF HYDROGEN IONS

Acid	Concn., moles per liter	$k_{obs.}$	k_0	$k_{obs.} - k_0$	$k_{H_3O^+}$
HCl	0.0004–0.002	0.0269	Av. value	....	...
HCl	0.004	.0269	....	....	...
HCl	.0240	.0274	0.0267	0.0007	0.027
HCl	.0443	.0281	.0267	.0014	$.031^5$
HCl	.0985	.0292	.0264	.0028	$.028^5$
HCl	.0984	.0294	.0264	.0030	$.030^5$
HCl	.149	.0309	$.0261^5$	.0049	.032
HCl	.198	.0320	$.0258^5$	$.0061^5$	.031
HCl	.198	.0322	$.0258^5$	$.0063^5$	.032
HCl	.248	.0338	.0256	.0082	.033
HNO_3	.0495	.0281	.0265	.0016	$.032^5$
HNO_3	.099	.0290	.0261	.0029	.029
$HClO_4$	.0738	.0285	.0261	.0024	$.032^5$
$HClO_4$	.148	.0299	.0252	.0047	.032
$HO_8SH_5C_6$	.0757	.0278	.0254	.0024	.032
$HO_3SH_5C_6$	.152	.0297	.0248	.0049	.032
				Av. =	0.031
				Average deviation =	5%

in the observed velocity constant means an error of 7% in $K_{H_3O^+}$ as determined from an experiment in 0.1 *N* acid, and an even greater error in the case of experiments in more dilute acid, the agreement in the values of $K_{H_3O^+}$ is very good.

In order to measure the acetate ion catalysis it is necessary to work in a sodium acetate–acetic acid buffer solution. Here the medium effect of k_0 of the non-electrolyte acetic acid and the salt effect of the sodium acetate must be known. Since 0.2 *M* sodium trichloro-acetate has the same effect as 0.2 *M* sodium chloride, we may assume the salt effect of sodium acetate to be the same as that of sodium chloride. Table IV and Fig. 4 show the medium effect of acetic acid upon the velocity constant.

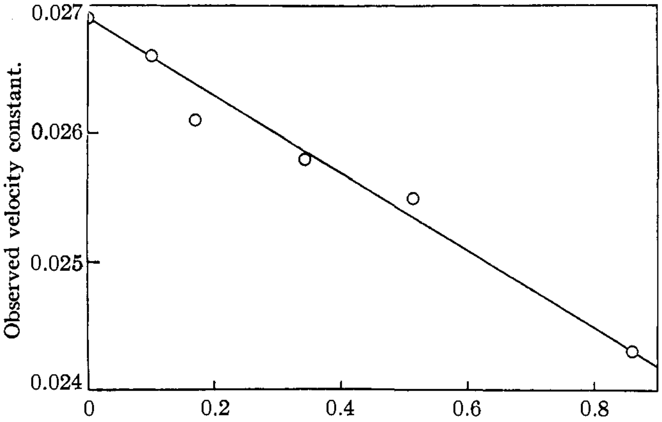


Fig. 4.—Effect of acetic acid.

TABLE IV

EFFECT OF ACETIC ACID

Init. concn. HAc, m./l.	0.000	0.100	0.170	0.343	0.514	0.860
k	.0269	.0266	.0261	.0258	.0255	.0243

These results may also be expressed by the equation $k_0 = 0.0269 - 0.0030\, m$, where *m* is the molarity of the acetic acid.

In Table V the results with sodium acetate–acetic acid buffers are given and K_{Ac} is calculated.

Here k'_0 (Col. 5) is k_0 corrected for the medium effect of the acetic acid and for the salt effect of the sodium acetate, upon the assumption that the two effects are additive. The corrected k_0 or k'_0 is then subtracted from the observed velocity constant, and the difference, divided by the acetate concentration, gives the constant of acetate ion catalysis. The concentration of acetate may be taken as equal to that of the sodium ion, since the hydrogen-ion concentration is less than 0.0002 M in all cases. An inspection of the acid–salt ratios in Table V shows that K_{Ac^-} is independent of the hydrogen-ion concentration. K_{Ac^-} is some 20% greater than $K_{H_3O^+}$.

TABLE V

EFFECT OF ACETATE

$NaOOCCH_3$, moles per liter	$HOOCCH_3$ moles per liter	NaCl, moles per liter	$k_{obs.}$	k'_0	$k - k'_0$	$k_{acetate}$
0.0495	0.236	0	0.0281	0.0261	0.0020	0.042
.0590	.112	0.139	.0281	.0256^5	.0024^5	.041^5
.0990	.025	0	.0306	.0264	.0042	.042
.0990	.115	0	.0294	.0262	.0032	.032
.0990	.233	0	.0291	.0257	.0034	.034
.0990	.117	.0990	.0294	.0256^5	.0037^5	.038
.0990	.188	.0990	.0292	.0252^5	.0039^5	.040
.0990	.044	.0990	.0297	.0257^5	.0039^5	.040
.119	.225	.0790	.0294	.0251^5	.0042^5	.035^5
.198	.232	0	.0327	.0250	.0077	.039
.198	.477	0	.0315	.0243	.0072	.036^5
.198	.232	0	.0331	.0251^5	.0079^5	.040
.198	.089	0	.0338	.256^5	.0081^5	.041^5
.198	.375	0	.0326	.0247	.0079	.040

Av. = 0.0385

Average deviation = 5%

Early experiments showed the formate ion to be a remarkably good catalyst, so good, in fact, that it was necessary to work at much lower concentrations of formate than of acetate and hydrogen ion. In studying the effect of formate ion the formic acid concentration must be sufficiently high so that the formate–formic acid buffer equilibrium is not appreciably displaced by the acetic acid which is formed during the course of the reaction. The results of the experiments in formate–formic acid buffer solution are summarized in Table VI.

TABLE VI

EFFECT OF FORMATE

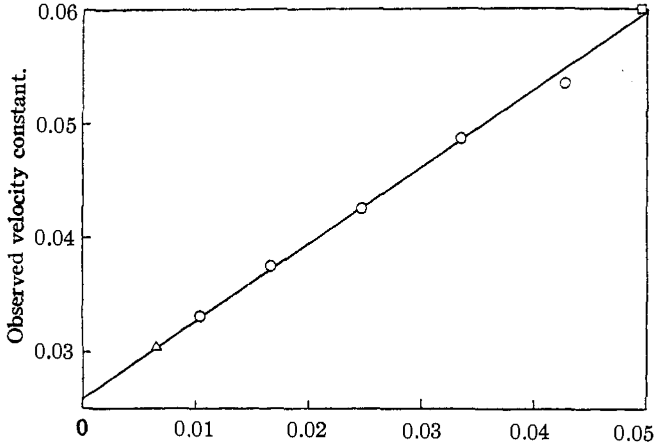
Composition of buffer							
Acid, moles/liter	Sodium salt, moles/liter	H^+, moles/liter	Formate, moles/liter	$k_{obs.}$	k	$k - k'$	$k_{formate}$
0.495	0	0.0104	0.0104	0.0331	0.0257	0.0074	0.712
.495	0.0099	.0067	.0166	.0375	.0256	.0119	.717
.495	.0198	.0049	.0247	.0426	.0255	.0171	.692
.495	.0297	.0038	.0335	.0488	.0255	.0233	.696
.495	.0396	.0031	.0427	.0536	.0254	.0282	.660
.198	0	.0063	.0063	.0304	.0263	.0041	.651
.024	.0495	.0003	.0498	.0591	.0266	.0325	.653
.120	.198	.0020	.200	.1564	.0255	.1309	.655

The formate-ion concentration (Col. 4) was calculated from the dissociation constant of formic acid, K_c, account being taken of the change in K_c with change in electrolyte concentration. For this purpose an equation given by Brönsted[16]

$$K_c = K_0 \frac{f_0}{f_1^2} = 1.8\ (1 + 2.36\ \sqrt{m})\ 10^{-4}$$

was used; in this equation m represents the molarity of a monomonovalent solvent salt. k', given in Col. 6, is k_0 corrected for the medium effect of formic acid (assumed to be equal to that of acetic acid, see Table IV) and for salt effect, and to this is added $K_{H_3O^+}[H_3O^+]$, or the amount of reaction due to the hydrogen-ion catalysis. The maximum total correction is 4%. In the last three experiments the concentration of formic acid was low and the observed velocity constant was obtained from the first part of the reaction.

In Fig. 5, $k_{obs.}$ is plotted against the formate-ion concentration.



Formic acid: ○, 0.495 mole/liter; △, 0.198 mole/liter; □, 0.024 mole/liter.

Fig. 5.—Effect of formate.

From the figure it is evident that the increase in rate of hydration or $k_{obs.} - k'$ is proportional to the formate-ion concentration. In other words, the acetic anhydride is disappearing by two paths as in the cases of hydrogen-ion and acetate-ion catalysis. The intercept on the axis of velocity constants is 0.0260, which represents the constant in a 0.495 M formic acid solution, the hydrogen-ion catalysis being included and the formate-ion catalysis excluded. The value chosen for k' on the assumption that the medium effect was the same as that of acetic acid was 0.0257.

It is to be noted that Szabó[7] does not report any catalytic effect of formate ion. She did no experiments, however, in sodium formate–formic acid buffer solution where the effect is very apparent.

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[16] Brönsted and Volquartz, *Z. physik. Chem.*, **134**, 109 (1928).

At 14° her velocity constants are: in water alone, 133.5×10^5 (time in seconds); in 2.07 *M* acetic acid, 85.9×10^5; in 2.07 *M* formic acid, 126.8×10^5. The medium effect of two molar acetic acid on k_0 is therefore 35% at 14°. Assuming the medium effect of acetic or formic acid on k_0 at 0° to be linear up to 2 *M* acid, the decrease amounts to 22%. In 2.1 *M* formic acid the formate-ion concentration is approximately 0.023 *M*. Since k_{formate} is 0.7, the formate-ion catalysis is 0.016, corresponding to a 60% increase in the velocity constant. Therefore, at 0° the rate of hydration in 2 *M* formic acid would be greater than that in water alone. Szabó found the opposite to be the case at 14°. Two explanations may be suggested: first, that the medium effect of formic acid on k_0 is greater at 14° than at 0° (which Szabó's figures indicate); and, second, that the temperature coefficient of the hydration in water alone is greater than the temperature coefficient of the formate-ion catalysis, that is

$$\frac{k_0^{14°}}{k_0^{0°}} > \frac{k_{\text{F}^-}^{14°}}{k_{\text{F}}^{0°}}$$

Szabó's few experiments in acetate buffer solution were made at such high salt concentrations that only an approximate value can be calculated for k_{Ac^-} at 18°. Expressing Szabo's constants in minutes^{-1} and using her salt effects, one gets $k_{\text{Ac}} = 0.10$ at 18° and $k_0 = 0.096$ at 18°, whence

$$\frac{k_0^{18°}}{k_0^{0°}} = \frac{0.096}{0.027} = 3.6 \text{ and } \frac{k_{\text{Ac}}^{18°}}{k_{\text{Ac}}^{0°}} = \frac{0.10}{0.039} = 2.6$$

When one considers the magnitude of k_{F^-} it is evident that there is no simple relationship between basic strength and catalytic efficiency as there is in the cases of the mutarotation of glucose and the decomposition of nitramide which will include both the formate and acetate ions. Since formate is a weaker base than acetate, k_{F^-} should be less than k_{Ac^-}; the value found is over fifteen times greater.

Experiments were also carried out in sodium propionate–propionic acid and sodium butyrate–butyric acid buffer solutions. In these solutions the reaction rate is slower than in water alone, as is shown by the results summarized in Tables VII and VIII.

TABLE VII

EXPERIMENTS IN PROPIONATE–PROPIONIC ACID BUFFER

Composition of Buffer			Composition of Buffer		
Acid moles/liter	Sodium salt, moles/liter	$k_{\text{approx.}}$	Acid, moles/liter	Sodium salt, moles/liter	$k_{\text{approx.}}$
0.304	0	0.0257^5	0.500	0.150	0.0184
.304	0	.0246[a]	.500	.200	.0174
.530	0	.0246	.250	.200	.0200
.500	0.0500	.0232	.125	.100	.0244
.500	.100	.0214	.150	.120	.0223

[a] In 0.2 *M* NaCl.

TABLE VIII

EXPERIMENTS IN BUTYRIC ACID–BUTYRATE BUFFER

Acid, mole/l.	0.50	0.50	0.50	0.50	0.50
Na salt, mole/l.	0	.050	.100	.150	.200
$k_{\text{approx.}}$	.0244	.0226	.0186	.0158	.0156

The reaction no longer exactly follows the monomolecular law and the constants have therefore been recorded as "approximate" in the tables. In addition, the contraction is much smaller.

From these results one may conclude that the acetic anhydride is no longer present wholly as such in the solution, but has combined with the propionate or butyrate to form an intermediate compound. The intermediate compound may be the mixed anhydride, for the rates of hydration are approximately the same as those calculated for the mixed anhydrides from the following considerations. Verkade has found 0.434 k for acetic anhydride at 25° to be 0.0713, the propionic anhydride 0.0372 and for the mixed anhydride 0.0524. The arithmetical mean of the constants for the simple anhydrides is 0.0542, which is approximately the constant determined for the mixed. Verkade's 0.434 k for propionic anhydride at 0° is 0.00700, and taking my value for acetic anhydride at 0° as 0.0117, the mean is 0.00935, or in terms of natural logarithms, 0.0215. In the absence of any actual determinations, 0.0215 may be taken as the approximate value of the constant for the mixed anhydride at 0°. In the fifth experiment of Table VII, that experiment in which there was a slight excess of propionate ion over acetic anhydride, the initial concentrations being 0.10 and 0.07 M, respectively, the constant found is 0.0214. According to a similar calculation for butyric acetic anhydride, k at 0° is 0.0189, while the value found in the third experiment of Table VIII is 0.0186. It must be mentioned, however, that before the kinetics of the hydration in solutions containing propionate or butyrate can be worked out, it will be necessary to know k_0, $k_{H_3O^+}$ k_{Ac^-} and possibly $k_{\text{propionate}}$ and k_{butyrate} for propionic and butyric anhydrides as well as for the mixed anhydrides, propionic-acetic and butyric-acetic.

There is considerable evidence[17] in the literature of organic chemistry for the formation of compounds between acetic anhydride and the carboxylic acids and their anions. Such compounds, however, have been formed under conditions quite different from those of the present experiments. The results of the experiments in formate-formic acid buffer solution do not preclude the formation of an unstable intermediate compound between the acetic anhydride and the formate ion.

The author wishes to thank the Rask-Ørsted Foundation, Copenhagen, for the grant which has made this work possible.

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[17] For discussion and further references see Autenrieth and Thomae, *Ber.*, **57B**, 423 (1924); Van der Haar, *Rec. trav. chim.*, **47**, 321 (1927); Verkade, *ibid.*, **37**, 331 (1918).

Summary

1. The velocity of hydration of acetic anhydride has been measured by a dilatometric method at 0°.

2. The salt effect on k_0 has been determined for a number of neutral salts in dilute solution. The medium effect of acetic acid has been measured.

3. The constants of hydrogen, acetate and formate-ion catalysis have been determined. The formate ion is a remarkably good catalyst.

4. In propionate–propionic acid and in butyrate–butyric acid buffer solutions the hydration is slower than in water alone. It is hoped to make a further study of this effect.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE INTERACTION BETWEEN NITROGEN TRICHLORIDE AND NITRIC OXIDE. REACTIONS OF COMPOUNDS WITH ODD ELECTRONS[1]

BY WILLIAM ALBERT NOYES

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In papers recently published,[2] the point of view has been presented that valence is a *unitary* atomic phenomenon. This is closely in accord with the original ideas of Frankland, Couper and Kekulé.

The endeavor has been made to show that for any given molecule, at any particular instant, the distinction between polar (or ionic) valences and covalences is sharp and definite. In the interest of clarity it has been proposed[3] to confine the term "polar valence" to the designation of valences which are actually ionic because of the complete transfer of an electron. The "semipolar" valences of oxygen in the sulfate radical, the amine oxides, etc., are, of course, half polar and half covalence.[4]

It has also been proposed to call those valences which have an electrical moment and which permit atoms held by a covalence to separate readily in the ionic form, "potentially polar," because the distinction between a covalence and an ionic valence is, theoretically, sharp and definite, while there may be all degrees of "potentially" polar valences.

This discussion seems to be a simple and logical development of the

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[1] In memory of Ira Remsen.

[2] (a) Noyes, *Z. physik. Chem.*, **130**, 325 (1927); (b) *Proc. Am. Phil. Soc.*, **66**, 299 (1927).

[3] Noyes, ref. 2 a, pp. 329; 26, 300.

[4] T. M. Lowry, *Trans. Faraday Soc.*, 19, 486 (1923); *J. Chem. Soc.*, **123**, 822 (1923); Sugden, *ibid.*, **125**, 1186 (1924); **127**, 1527 (1925); Harrison, Kenyon and Phillips, *ibid.*, **129**, 2079 (1926); Noyes, THIS JOURNAL, **47**, 3027, footnote (1925); *Z. physik. Chem.*, **130**, 327 (1927).