

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE TEMPERATURE COEFFICIENT OF REACTIONS CATALYZED BY ACIDS AND BASES¹

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Although considerable effort has been devoted to the detection and study of reactions showing general acid and basic catalysis,² little is known of the change, with change in temperature, of the rates of the catalyzed reactions. In the case of a reaction catalyzed by acids HA_1, HA_2, \dots and by bases A_1, A_2, \dots it is unlikely that the energies of activation $E_{HA_1}, E_{HA_2}, \dots, E_{A_1}, E_{A_2}, \dots$ are all equal. It is, therefore, to be expected that the relationship between catalytic strength and acid (or basic) strength would change with change in temperature.

It is generally accepted that, in ester hydrolysis, the temperature coefficient of the hydroxyl-ion catalyzed reaction is lower than that of the hydrogen-ion catalyzed reaction. The same is probably true of the hydrolysis of the amides, in spite of the discrepancies between the experimental results of different workers. In the case of the mutarotation of glucose, Hudson and Dale³ report that the energy of activation of the water reaction is practically the same as that of the hydrogen-ion catalyzed reaction. The hydration of acetic anhydride, which proceeds rapidly in water, is catalyzed by hydrogen and hydroxyl ions, and by the anions of formic and acetic acids.⁴ Using the velocity constants of Szabó,⁵ at 18°, and his own at 0°, Kilpatrick estimated for the temperature coefficient of the reaction in water alone

$$k_0^{18^\circ}/k_0^{0^\circ} = 3.6$$

and for the catalysis by the acetate ion

$$k_{A_0}^{18^\circ}/k_{A_0}^{0^\circ} = 2.6$$

The reaction between acetone and iodine in aqueous solution has been found by Dawson⁶ to show general acid and basic catalysis. This work was carried out at 25°. Rice and his co-workers, however, investigated the reaction (considered simply as catalysis by the hydrogen ion) at different

¹ Paper presented at the Buffalo meeting of the American Chemical Society, September, 1931.

² For references, see Brønsted, *Trans. Faraday Soc.*, **24**, 630 (1928).

³ Hudson and Dale, *THIS JOURNAL*, **39**, 320 (1917).

⁴ Kilpatrick, *ibid.*, **50**, 2891 (1928).

⁵ Szabó, *Z. physik. Chem.*, **122**, 405 (1926).

⁶ For the earlier references, see Dawson, *Trans. Faraday Soc.*, **24**, 640 (1928); Dawson, Hoskins and Smith, *J. Chem. Soc.*, 1884 (1929); Dawson and Smith, *ibid.*, 79 (1930); Dawson and Spivey, *ibid.*, 2180 (1930).

temperatures.⁷ Recently Rice and Urey⁸ have suggested that the decrease observed in the temperature coefficient of the acetone-iodine reaction catalyzed by sulfuric acid, when sodium sulfate is added, is to be attributed to the fact that with addition of the salt a greater part of the original acid is present as bisulfate ion, and to the fact that the temperature coefficient of the bisulfate-ion catalyzed reaction is less than that of the hydrogen-ion catalyzed reaction. They assign a value of 17,100 calories to the energy of activation of the bisulfate-ion catalyzed reaction; that of the hydrogen-ion catalyzed reaction, as determined from experiments in dilute hydrochloric acid solution, is 20,540 calories.

The temperature coefficient of the hydrogen-ion catalyzed reaction was determined by making separate experiments at two temperatures, and also by the "two-thermostat" method, in which portions of the same solution were used for carrying out experiments at two temperatures, simultaneously, the temperature coefficient being obtained directly from the ratio of the rates of disappearance of iodine. The two methods gave values in good agreement.^{7a} The heats of activation of the acetone-iodine reaction catalyzed by 0.1 *N* sulfuric acid, by 0.1 *N* sulfuric acid in the presence of 0.434 *M* sodium sulfate and by 0.1 *N* sulfuric acid in the presence of 0.87 *M* sodium sulfate were obtained from independent experiments carried out at 23 and 25°. Those for the reaction catalyzed by 0.15 *N* sulfuric acid in the presence of 0.05 *M* sodium sulfate and by 0.097 *N* sulfuric acid in the presence of 1.69 *M* ammonium sulfate were obtained by the two-thermostat method, a five-degree temperature interval being used. In the former set of experiments with sulfuric acid as catalyst, the velocity constants are probably consistent to 0.2%, corresponding to a precision measure of 0.9% in the heat of activation. The published results, however, are not in agreement with the experimentally determined values.⁹ The discrepancies appear to be due, in the main, to an error in the calculation.¹⁰ These errors in calculation do not invalidate the conclusion of Rice and Lemkin that the temperature coefficient of the acetone-iodine reaction catalyzed by sulfuric acid is less than that of the reaction catalyzed by hydrochloric acid, and that the addition of sodium sulfate causes a further depression. They do, however, make the total change in the heat of activation 2500 calories rather than 3500.

Provided the catalytic effect of the sulfate ion is negligible, the velocity

⁷ (a) Rice and Kilpatrick, *THIS JOURNAL*, **45**, 1401 (1923); (b) Rice and Lemkin, *ibid.*, **45**, 1896 (1923); (c) Rice and Fryling, *ibid.*, **47**, 379 (1925).

⁸ Rice and Urey, *ibid.*, **52**, 95 (1930).

⁹ Lemkin, Dissertation, New York University, 1922.

¹⁰ In converting the velocity constant per 1000 g. of solution to the velocity constant per liter, Rice and Lemkin have apparently divided by the density rather than multiplied. Consequently the heats of activation are in error; the error in some cases is almost 1000 calories.

of the acetone-iodine reaction in sulfuric acid solution is

$$-dc_{I_2}/dt = (k_{H_3O^+} c_{H_3O^+} + k_{HSO_4^-} c_{HSO_4^-})c_{acetone}$$

where $k_{H_3O^+}$ and $k_{HSO_4^-}$ represent the catalytic constants, at the electrolyte concentration in question, of molar hydrogen and bisulfate ion, respectively. The velocity constant employed by Rice and his co-workers is that given by the equation

$$-dc_{I_2}/dt = k_{obs.}(c_{H_3O^+} + c_{HSO_4^-})c_{acetone}$$

Calling the last-mentioned the "observed" velocity constant

$$k_{obs.} = (k_{H_3O^+} c_{H_3O^+} + k_{HSO_4^-} c_{HSO_4^-}) / (c_{H_3O^+} + c_{HSO_4^-})$$

Since the reaction is slower in 0.1 *N* sulfuric acid solution than in 0.1 *N* hydrochloric acid solution, the catalytic constant of the bisulfate ion is less than that of the hydrogen ion; Rice and Urey assign to $k_{HSO_4^-}$ in 0.1 *N* sulfuric acid solution a value of 12.6×10^{-4} , whereas $k_{H_3O^+}$ is 17.1×10^{-4} . Since $k_{HSO_4^-} \rightleftharpoons k_{H_3O^+}$, it follows that the observed velocity constant must change as the ratio $c_{H_3O^+}/c_{HSO_4^-}$ changes. Therefore, quite apart from electrolyte effect on $k_{H_3O^+}$ and $k_{HSO_4^-}$, the statement of Rice and Urey that ". . . the specific," *i. e.*, observed, "velocity constant should not change with a variation of the concentration of the sulfuric acid, in agreement with observation" cannot be correct. The observed velocity constant, moreover, must change during the course of an experiment with change in the $c_{H_3O^+}/c_{HSO_4^-}$ ratio brought about by the formation of hydriodic acid. While experiments over any considerable range of sulfuric acid concentration are not available, it may be mentioned that for 0.08063 *N* sulfuric acid at 25° Kilpatrick¹¹ obtained a velocity constant of 15.54×10^{-4} ; for 0.09657 *N* acid Lemkin¹² obtained a value of 15.27×10^{-4} ; while for 0.1175 *N* acid Fryling¹³ found 14.32×10^{-4} and for 0.1539 *N* acid, 14.38×10^{-4} .

In order to be useful for our purpose, a reaction should be catalyzed by a number of acids and bases of diversified types. It should not have so fast a water reaction, nor should it be so sensitive to the hydrogen or hydroxyl ion, as to make difficult the determination of the effects of other catalysts. In other words, the slope of the line obtained by plotting the logarithm of the catalytic constant against the logarithm of the dissociation constant for the acids, or for the bases, which catalyze a reaction must not be too flat (in which case the water reaction predominates), nor must it be too steep (in which case the hydrogen-ion, or hydroxyl-ion, effect masks all other effects).² The reaction must also be one which can be followed conveniently.

¹¹ Kilpatrick, Dissertation, New York University, 1923.

¹² The figure given is recalculated from data in the dissertation of Lemkin, New York University, 1922.

¹³ Fryling, Dissertation, New York University, 1923.

The acetone-iodine reaction possesses a number of advantages. Its rate is convenient, and the velocity constant of the reaction catalyzed by strong acids can be obtained with great accuracy.^{7a} Using Dawson's values of the catalytic constants of a number of acids and bases, we have plotted the logarithm of the catalytic constant against that of the dissociation constant; the slope of the $\log k_A - \log K_A$ line is about 0.4, that of the $\log k_B - \log K_A$ line is -0.6 , *i. e.*, the reaction is favorable for the detection of catalytic effects in general. But the acetone-iodine reaction also has disadvantages. When the hydrogen-ion concentration is low, iodoform is produced as well as acetone. And due to the fact that hydriodic acid is a product of the reaction, it is difficult to obtain accurate results in dilute buffer solutions.

The mutarotation of glucose shows general acid and basic catalysis.¹⁴ The reaction obeys a pseudo-monomolecular law, and may be conveniently followed polarimetrically or dilatometrically. The primary salt effect, as Brönsted and Guggenheim have shown, is small. Although the water reaction is large, it is possible to determine the catalytic effects of acids and bases over a considerable range of acid strength. The chief disadvantage of the mutarotation, for a temperature coefficient study, is that at 25° the water reaction is fast enough to make it difficult to evaluate the catalytic effects with accuracy.

Because of the possibility of determining its temperature coefficient when catalyzed by acids and bases of quite different types, we have chosen for study the mutarotation of glucose.

Experimental Part and Discussion of Results

Three lots of α -glucose were used—Pfanstiel's, Eastman's and a lot which we prepared in the laboratory according to the directions of Hudson and Dale.⁸ No difference in velocity of mutarotation was observed between the three.

The reaction was followed dilatometrically. The velocity constants were calculated by Guggenheim's¹⁵ method.

The temperature coefficient k_{25}/k_{20} was obtained by the two-thermostat method, *i. e.*, experiments were carried out simultaneously at the two temperatures with portions of the same solution. The thermostats in which the dilatometers stood were regulated to 20 and $25 \pm 0.003^\circ$, respectively, the temperature interval being checked by means of a calibrated resistance thermometer. The method of carrying out the experiments was essentially the same as that of Brönsted and Guggenheim and need not be described further. There are, however, a number of observa-

¹⁴ (a) Brönsted and Guggenheim, *THIS JOURNAL*, 49, 2554 (1927); (b) Lowry and Smith, *J. Chem. Soc.*, 2539 (1927).

¹⁵ Guggenheim, *Phil. Mag.*, 1, 538 (1926).

tions worth recording. In most cases it is more convenient to fill a dilatometer by pressure rather than by suction. In the case of the glucose reaction, however, the addition of glucose (10%) lowers the dielectric constant of the solution to such an extent that the dissolved gases tend to separate out in the dilatometer. To avoid this, it is necessary to remove a part of the dissolved gases by suction before filling the dilatometer. Brönsted and Guggenheim reported that the first readings seemed to be low and attributed this to drainage down the wall of the capillary. Our dilatometers were equipped with screw plungers¹⁶ so that it was not necessary to run the solution to the top of the capillary. Nevertheless, we found the same effect and believe it to be due to difference in temperature between the reacting solution and the bath. Although Brönsted and Guggenheim were careful to bring the solution into thermal equilibrium with the bath, they afterward applied suction, which would have a cooling effect.

Table I gives the values of the temperature coefficient of the mutarotation in hydrochloric acid solution. The velocity constants are in terms of natural logarithms, and min.^{-1} . From the temperature coefficient the energy of activation, E , has been calculated by means of the Arrhenius equation; its value in calories is recorded in the last column of the table.

TABLE I
THE TEMPERATURE COEFFICIENT IN HYDROCHLORIC ACID SOLUTION

HCl, moles per liter	$k_{\text{obs.}, 25^\circ}$	$k_{\text{obs.}, 20^\circ}$	k_{25}/k_{20}	E
0.05	0.0648	0.0368	1.761	19,600
.04	.0556	.0315	1.765	19,700
.02	.0403	.0233	1.729	19,000

In the hydrochloric acid solutions the mutarotation proceeds by two paths, (1) by way of the water reaction, and (2) by way of the hydrogen-ion catalyzed reaction. The velocity constant of the water reaction at 25° is 0.0253, so that in the first experiment about 60% of the total reaction went by way of the hydrogen-ion path, and in the last experiment a little less than 40%.

Table II gives a set of results obtained in sodium acetate-acetic acid buffer solutions.

TABLE II
THE TEMPERATURE COEFFICIENT IN ACETATE-ACETIC ACID BUFFER SOLUTIONS

Moles per liter		$k_{\text{obs.}, 25^\circ}$	$k_{\text{obs.}, 20^\circ}$	k_{25}/k_{20}	E
CH_3COONa	CH_3COOH				
0.20	0.26	0.0582	0.0352	1.653	17,500
.16	.21	.0524	.0304	1.724	18,900
.080	.10	.03935	.0224	1.756	19,500
.040	.051	.0334	.0192	1.740	19,200

¹⁶ Kilpatrick, *THIS JOURNAL*, 50, 2891 (1928).

In these experiments there were small catalytic effects of the hydrogen and hydroxyl ion (< 0.1%) and of the acetic acid molecule (< 4%); since portions of the same solution were used, $k_{\text{obs.}, 25^\circ}$ and $k_{\text{obs.}, 20^\circ}$ would be affected to practically the same extent. At the highest acetate concentration about 55% of the total reaction went by way of the acetate path, and at the lowest, about 25%.

Table III gives the results obtained in pyridine-pyridinium chloride buffer solutions.

TABLE III

TEMPERATURE COEFFICIENT IN PYRIDINE-PYRIDINIUM CHLORIDE BUFFER SOLUTIONS

Moles per liter		$k_{\text{obs.}, 25^\circ}$	$k_{\text{obs.}, 20^\circ}$	k_{25}/k_{20}	E
$\text{C}_5\text{H}_5\text{N}$	$\text{C}_5\text{H}_5\text{NCl}$				
0.050	0.025	0.0481	0.0270	1.78 ₁	20,000
.038	.018	.0417	.0236	1.767	19,800
.025	.013	.0365	.0203	1.798	20,400
.013	.0063	.0313	.0184	1.70 ₁	18,400

Any catalytic effect of the pyridinium ion is negligible.^{14a} The part of the reaction going by way of the pyridine path decreased from 45 to 20%, but there is no regular change in the temperature coefficient as would be expected if the heat of activation of the pyridine-glucose collision complex were markedly different from that of the glucose-water complex.

The same is true of the results given in Tables I and II. The average deviation of the temperature coefficient from the mean is 2%, corresponding to an average deviation of 1000 calories in E . In order to get E more accurately, experiments were performed at 0° and the catalytic constants were evaluated separately in each case.

The experiments at 0° were carried out in the dilatometer previously used for the study of the rate of hydration of the acid anhydrides.¹⁶ Although, due to the size of the dilatometer, the volume change was small, the reaction was so much slower that the difficulties arising from lack of thermal equilibrium disappeared.

Tables IV, V and VI give the catalytic constants of the hydrogen ion, the acetate ion and pyridine, respectively, at 0°. At this temperature the velocity constant of the water reaction, k_0 , is 0.00169.

TABLE IV

THE CATALYTIC EFFECT OF THE HYDROGEN ION AT 0°

HCl, moles per liter	$k_{\text{obs.}}$	$k_{\text{obs.}} - k_0$	$k_{\text{H}_3\text{O}^+}$
0.0500	0.00375	0.00206	0.0414°
.100	.00538	.00369	.0369
.124	.00630	.00461	.0372
.249	.01113	.00944	.0379

Average, 0.0373

Av. dev. 1%

° Omitted from the average.

TABLE V
THE CATALYTIC EFFECT OF THE ACETATE ION AT 0°

Moles per liter		$k_{obs.}$	$k_{obs.} - k_0$	k_{Ac^-}
CH_3COONa	CH_3COOH			
0.0400	0.050	0.00205	0.00036	0.0090
.0800	.10	.00250	.00081	.0101
.160	.21	.00304	.00135	.0084
.200	.26	.00350	.00181	.0090
Average, 0.0091				
Av. dev. 5%				

TABLE VI
THE CATALYTIC EFFECT OF PYRIDINE AT 0°

Moles per liter		$NaCl$, moles per liter	$k_{obs.}$	$k_{obs.} - k_0$	k_{Py}
C_5H_5N	C_5H_5NCl				
0.250	0.050	0	0.00890	0.00721	0.0288
.200	.040	0.010	.00777	.00608	.0304
.0500	.010	0.040	.00331	.00162	.0324
.250	.25	0	.00920	.00751	.0300
.175	.18	0	.00708	.00539	.0308
.125	.13	0	.00563 ₅	.00393 ₅	.0316
.0750	.075	0	.00404	.00235	.0314
Average, 0.0308					
Av. dev. 3%					

Between the two sets of experiments in pyridine-pyridinium chloride buffer solution there was a five-fold difference in hydrogen-ion concentra-

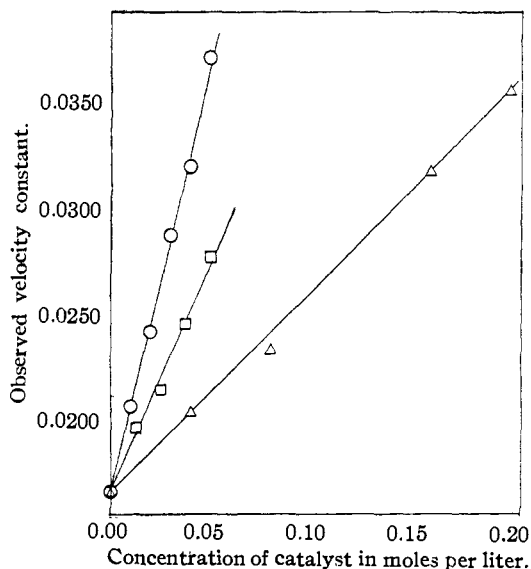


Fig. 1.—Effect of catalyst at 20°: ○, H_3O^+ ; □, pyridine; △, acetate.

tion. As can be seen from the table, the effects of hydrogen and hydroxyl ion are not detectable over this range. Since an error of 2% in $k_{obs.}$ means an error of 4% in k_{Py} for the lowest pyridine concentration, the agreement is satisfactory. With the acetate buffers an error of 2% in $k_{obs.}$ causes an error of more than 10% in k_{Ac^-} for the lowest acetate concentration.

Figure 1 presents these results graphically and shows the proportionality between the increase in the observed velocity constant and the concentration of catalyst.

The intercept on the axis of velocity constants is the velocity constant of the water reaction.

Similarly Tables VII, VIII and IX give the catalytic constants of the hydrogen ion, the acetate ion and pyridine at 20°. Here the velocity constant of the water reaction is 0.0152.

TABLE VII
THE CATALYTIC EFFECT OF THE HYDROGEN ION AT 20°

HCl, moles per liter	$k_{obs.}$	$k_{obs.} - k_0$	$k_{H_3O^+}$
0.0100	0.0195	0.0043	0.43
.0200	.0233	.0081	.405
.0300	.0281	.0129	.430
.0400	.0315	.0163	.408
.0500	.0368	.0216	.432
			Average, 0.421
			Av. dev. 4%

TABLE VIII
THE CATALYTIC EFFECT OF THE ACETATE ION AT 20°

Moles per liter		$k_{obs.}$	$k_{obs.} - k_0$	k_{Ac^-}
CH_3COONa	CH_3COOH			
0.0400	0.050	0.0192	0.0040	0.10
.0800	.10	.0224	.0072	.090
.160	.21	.0313	.00161	.101
.200	.26	.0352	.00200	.100
			Average, 0.098	
			Av. dev. 4%	

TABLE IX
THE CATALYTIC EFFECT OF PYRIDINE AT 20°

Moles per liter		$k_{obs.}$	$k_{obs.} - k_0$	k_{Py}
C_5H_5N	C_5H_5NCl			
0.0500	0.025	0.0270	0.0118	0.236
.0375	.018	.0236	.0084	.224
.0250	.013	.0203	.0051	.204
.0125	.0063	.0184	.0032	.256
			Average, 0.230	
			Av. dev. 7%	

These results are shown in Fig. 2. Again the increase in $k_{obs.}$ is proportional to the concentration of catalyst.

TABLE X
THE CATALYTIC EFFECT OF THE HYDROGEN ION AT 25°

HCl, moles per liter	$k_{obs.}$	$k_{obs.} - k_0$	$k_{H_3O^+}$
0.0500	0.0648	0.0395	0.790
.0400	.0556	.0303	.758
.0200	.0403	.0150	.750
			Average, 0.766
			Av. dev. 2%

TABLE XI
THE CATALYTIC EFFECT OF THE ACETATE ION AT 25°

Moles per liter		$k_{\text{obs.}}$	$k_{\text{obs.}} - k_0$	k_{Ac^-}
CH_3COONa	CH_3COOH			
0.0400	0.050	0.0334	0.0081	0.202
.0800	.10	.03935	.0140	.175
.160	.21	.0524	.0271	.170
.200	.26	.0582	.0329	.164
				Average, 0.178
				Av. dev., 6%

TABLE XII
THE CATALYTIC EFFECT OF PYRIDINE AT 25°

Moles per liter		$k_{\text{obs.}}$	$k_{\text{obs.}} - k_0$	k_{Py}
$\text{C}_5\text{H}_5\text{N}$	$\text{C}_5\text{H}_5\text{NCl}$			
0.0500	0.025	0.0481	0.0228	0.456
.0375	.018	.0417	.0164	.437
.0250	.013	.0365	.0112	.448
.0125	.0063	.0313	.0060	.480
				Average, 0.455
				Av. dev., 3%

Tables X, XI and XII and Fig. 3 give the results at 25°. The velocity constant of the water reaction at 25° is 0.0253.

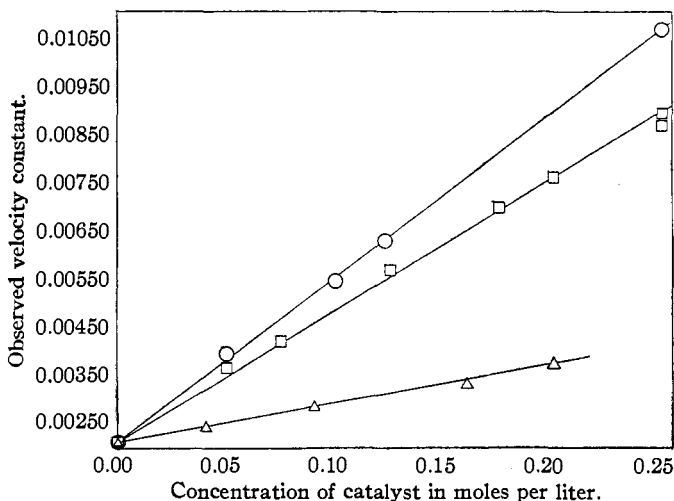


Fig. 2.—Effect of catalysts at 0°: ○, H₂O⁺; □, pyridine; △, acetate.

In evaluating the catalytic constant of the acetate ion at the three temperatures, we have neglected the effect of the molecular acetic acid. This effect, as a matter of fact, is not detectable in our results.¹⁷

¹⁷ See also the experiments of Brønsted and Guggenheim,^{14a} Table V and Figure 3A.

In Fig. 4 the logarithms of the catalytic constants, and of k_0 are plotted against the reciprocal of the absolute temperature. The values of k_0 which we obtain are in good agreement with those of Hudson and Dale. Included on the plot are the results of Brönsted and Guggenheim at 18°, which (after conversion to the base e) are

$k_{\text{H}_3\text{O}^+}$	= 0.331	Av. dev. 6%
k_{Ac^-}	= 0.0680	Av. dev. 4%
k_{Py}	= 0.192	Av. dev. 3%
k_0	= 0.0122	

The slopes of the lines in Fig. 4, multiplied by 4.574, give the values of the heat of activation listed in Table XIII.

TABLE XIII
HEATS OF ACTIVATION

Catalyst.....	Hydrogen ion	Acetate ion	Pyridine	Water
Heat of activation.....	19,300	19,100	18,000	17,600

In the case of pyridine, the catalytic constant at 0° is high in comparison with the values at 18, 20 and 25°, making poor the conformity to the line of Fig. 4. In the two sets of experiments carried out at 0°, however, the considerable difference in the pyridinium ion concentration and in the buffer ratio caused no appreciable change in k_{Py} .

In order to test further the idea of change in the heat of activation with change in catalyst, a few experiments were carried out with another reaction which shows general acid catalysis, namely, the hydrolysis of ethyl orthoacetate.¹⁸ The rate was measured in sodium *p*-nitrophenolate-*p*-nitrophenol buffer solutions at constant ionic strength. The water reaction is negligible, and by dilution of the buffer at constant ionic strength that part of the reaction going by way of the hydrogen ion was kept constant while the part going by way of the molecular *p*-nitrophenol decreased.

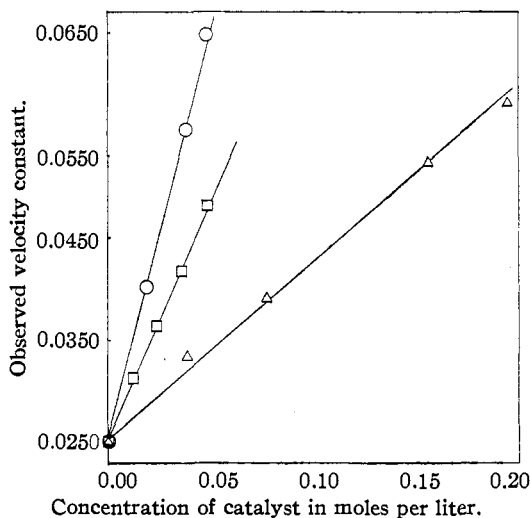


Fig. 3.—Effect of catalysts at 25°: O, H₃O⁺; □, pyridine; Δ, acetate.

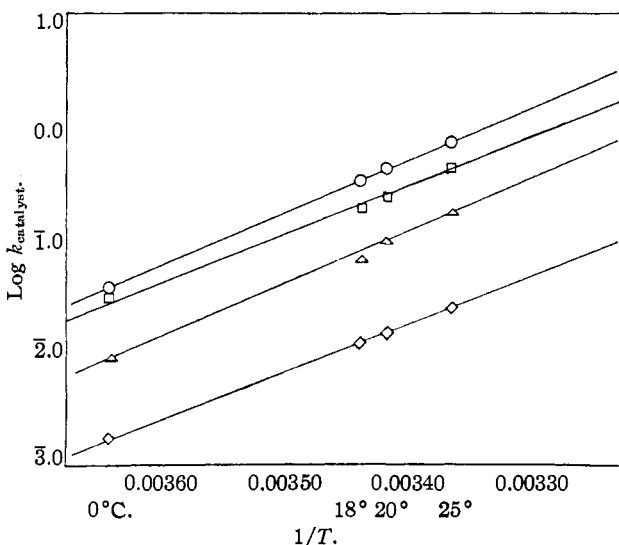
¹⁸ Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, 25, 59 (1929).

TABLE XIV

THE TEMPERATURE COEFFICIENT OF THE HYDROLYSIS OF ETHYL ORTHOACETATE

Moles per liter			$k_{\text{obs.}, 25^\circ}$	$k_{\text{obs.}, 20^\circ}$	k_{25}/k_{20}	E
<i>p</i> -Nitrophenol	Na salt	NaCl				
0.0100	0.0500	0	0.0514	0.0291	1.766	19,700
.00750	.0375	.0125	.0481	.0273	1.762	19,700
.00500	.0250	.0250	.0462	.0262	1.763	19,700
.00250	.0167	.0333	.0445	.0260	1.712	18,700

The observed velocity constants were plotted against the *p*-nitrophenol concentration and the intercepts on the axis of velocity constants gave $c_{\text{H}_3\text{O}^+} k_{\text{H}_3\text{O}^+}$ as 0.0423 at 25° and 0.024 at 20°. Provided there is no appreciable change in the dissociation constant of the acid over this interval, the temperature coefficient of the hydrogen-ion catalyzed reaction is 1.76, which corresponds to a heat of activation of 19,600 calories.

Fig. 4.—○, H_3O^+ ; □, pyridine; △, acetate; ◇, water.

In the first experiment of Table XIV about 20% of the total reaction went by way of the *p*-nitrophenol, in the last, 5%. In order to yield a change of 1000 calories, the values of the heat of activation by the two paths would have to differ by 7000 calories. That is to say, for the purpose in hand the reaction is not a suitable object of study over a short temperature interval. It is relatively so sensitive to the hydrogen ion that the determination of the effects of other acid catalysts is difficult. Salt effects are troublesome. Due to the extreme sensitivity to the hydrogen ion, alteration of the buffer medium by dilution at constant ionic strength is dangerous. The primary salt effects on the hydrogen-ion catalyzed, and on the acid-molecule catalyzed reaction may be considerable.

In this connection it may be mentioned that we have measured the rate of hydrolysis of an analogous compound, ethyl orthocarbonate, in solutions of high and constant salt concentration where the concentration of buffer salt was so small a fraction of the total salt concentration that the medium may be considered constant. Experiments in sodium cacodylate-cacodylic acid buffer solutions at $\mu = 1.1$, sodium chloride contributing over 90% of the ionic strength, showed proportionality between the increase in velocity constant and increase in cacodylic acid concentration in quite the same way as experiments at $\mu = 0.1$. The primary salt effect on the cacodylic-acid catalyzed reaction is very large. At 20° and $\mu = 0.1$ k_{HCac} is 0.030,¹⁹ at $\mu = 1.1$ (mostly NaCl) k_{HCac} is 0.011,¹⁹ while for $\mu = 0.025$ and $\mu = 0.05$ Brönsted and Wynne-Jones give an average value of 0.039. The magnitude of the electrolyte effect varies considerably from reaction to reaction.²⁰ The effect just cited is very large. On the other hand, in the case of the acetone-iodine reaction Dawson finds very little change, over an extended range of electrolyte concentration, in the catalytic constant of molecular acetic acid.²¹

It has already been mentioned that, for reactions showing general acid or basic catalysis, a linear relationship is expected between the logarithm of the catalytic constant and the logarithm of the dissociation constant of the catalyzing acid or base. On the assumption that for a given temperature, medium and reaction the catalytic constant k_A is proportional to the velocity constant of the dissociation of the catalyzing acid, and on the assumption that an increase in the dissociation constant K_A , for a series of analogous acids, is brought about by an increase in the rate of dissociation and a simultaneous decrease in the rate of association, Brönsted proposed the equation

$$k_A = G_1 K_A^x$$

where G_1 and x are constants and $1 > x > 0$. For reactions catalyzed by bases he proposed the analogous equation

$$k_B = G_2 K_B^y$$

In the decomposition of nitramide,²² and in the acetone-iodine reaction,²³ these equations have been found to hold exactly for catalysts of the same type. They have been found to hold approximately, over a range of 18 powers of ten in K_A , in the mutarotation of glucose^{14a} and in the hydrolysis of ethyl orthoacetate, ethyl orthopropionate and ethyl orthocarbonate.¹⁸

Since no reaction has been examined at several temperatures with suffi-

¹⁹ These experiments were carried out, under our direction, by Mr. Lester W. Strock.

²⁰ Brönsted and Grove, *THIS JOURNAL*, **52**, 1394 (1930); Kilpatrick and Chase, *ibid.*, **53**, 1732 (1931).

²¹ Dawson, *Trans. Faraday Soc.*, **24**, 640 (1928).

²² Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

²³ Dawson, Hoskins and Smith, *J. Chem. Soc.*, 1884 (1929).

cient thoroughness, it is not known whether the slope of the line obtained by plotting the logarithm of the catalytic constant against that of the dissociation constant changes with temperature, or not. Assuming that the changes in the dissociation constants with temperature are small, one sees that if the heats of activation for the different catalysts are the same, the slope of the line remains constant, and that if the heats of activation change regularly with the acid or basic strength of the catalyst, the slope changes with temperature. We have determined at 0, 20 and 25° the catalytic effects of the hydrogen ion, the acetate ion and pyridine on the mutarotation of glucose, and have measured the rate of the water reaction. In the group are three basic catalysts of different type—the acetate ion, pyridine, and water—and two acid catalysts of different type—the hydrogen ion and water. If these can be taken as representative, in the case of the mutarotation of glucose little change in the relationship between catalytic strength and the relative acid strength is to be expected with change in temperature.

Summary

1. The catalytic effects of the hydrogen ion, the acetate ion and pyridine on the mutarotation of glucose have been determined at 0, 20 and 25°, and the rate of the water reaction has been determined at these temperatures.

2. Within the experimental error of the measurements, the heats of activation are the same for the reaction catalyzed by the hydrogen ion and by the acetate ion. The heat of activation for the mutarotation in water alone appears lower.

3. The results have been discussed from the point of view of the relationship between the catalytic constant and the dissociation constant of the catalyzing acid or base.

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