[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

CONTRIBUTION TO THE THEORY OF ACID AND BASIC CATALYSIS. THE MUTAROTATION OF GLUCOSE

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1. Introduction. The Conception of Acids and Bases

According to an extended conception of acids and bases,[1] a molecule, whether neutral or electrically charged, is defined as being an acid if it has a tendency to split off a hydrogen nucleus and as being a base if it has a tendency to unite with a hydrogen nucleus. If we compare the balanced reactions

$$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$$
$$NH_4^+ \rightleftharpoons NH_3 + H^+$$
$$[Co(NH_3)_5OH_2]^{+++} \rightleftharpoons [Co(NH_3)_5OH]^{++} + H^+$$

the fact that some of the molecules are neutral and others electrically charged is trivial in comparison with the fundamental similarity of the three equilibria. In general we may write the acid-base equilibria as

$$A \rightleftharpoons B + H^+$$

where A is an acid and B the conjugate base; A and B may have any electrical charge, positive, zero or negative, but naturally that of the acid A is always one greater algebraically than that of the conjugate base B. It is of course possible for a molecule to be both an acid and a base; an obvious example is OH_2 which is an acid according to the scheme

$$OH_2 \rightleftharpoons OH^- + H^+$$

the conjugate base being OH^-, whereas it is a base according to the scheme

$$OH_3^+ \rightleftharpoons OH_2 + H^+$$

the conjugate acid being OH_3^+, the form in which the so-called hydrogen ion is present in aqueous solution; we shall always call OH_3^+ "oxonium" when we wish to distinguish it sharply from H^+ which we shall then call "proton."

We accordingly see that basic properties are common to all molecules tending to combine with a proton and hydroxyl is in no way unique except for the fact that in aqueous solution its conjugate acid is the solvent molecule. Similarly, since the proton does not exist in solution, the so-called "hydrogen ions" are different chemical molecules in different solvents and these various solvated hydrogen ions are in no way different from other acid molecules, except for the fact that the conjugate bases are the solvent molecules.

We shall not in the present paper enter into the important question of a general measure of the strength of acids and bases[2] and its dependence

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[1] (a) Brönsted, *Rec. trav. chim.*, **42**, 718 (1923); (b) *J. Phys. Chem.*, **30**, 777 (1926).

[2] See Brönsted, Om Syre-og Basekatalyse, *Festskrift*, Københavns Universitat, **1926**.

on the solvent. In dilute aqueous solution, however, at a given temperature the strength of an acid A might be measured by the equilibrium constant K_A' of the process defining the acid; that is, K_A' is the limiting value at infinite dilution of the ratio $c_B \cdot c_{H^+}/c_A$ in which c_B, c_{H^+} and c_A are equilibrium values of the concentrations of B, H^+ and A, respectively. Owing to the fact that c_{H^+} is practically infinitesimal, K_A' is a purely formal quantity whose absolute value is too small to be measured. We can, however, also quite formally attribute an equilibrium constant K° to the process defining the acid property of oxonium ion; thus $K^\circ = c_{OH_2} \cdot c_{H^+}/c_{OH_3^+}$ where c_{OH_2}, c_{H^+} and $c_{OH_3^+}$ are equilibrium values of the concentrations of OH_2, H^+ and OH_3^+, respectively. Then the strength of the acid A relative to oxonium may be measured by the ratio K_A'/K° or $c_B \cdot c_{OH_3^+}/c_A \cdot c_{OH_2}$, which is the mass action constant of the actual double acid-base equilibrium in the solution. But as in dilute aqueous solution c_{OH_2} is constant we can equally well measure the relative strength of an acid A by the ratio $c_B \cdot c_{OH_3^+}/c_A$. This we shall call the acid constant and denote it by K_A. We shall find it convenient to measure the strength of the conjugate base B by the reciprocal of K_A; this we shall call the basic constant of B and denote it by K_B.

For such an acid as acetic acid, K_A is identical with the ordinary electrical dissociation constant in water $c_{Ac^-} \cdot c_{OH_3^+} = c_{AcH}$. For such an acid as ammonium ion we have

$$K_A = \frac{c_{NH_3}\, c_{OH_3^+}}{c_{NH_4^+}} = c_{OH_3^+} \cdot c_{OH^-} \cdot \frac{c_{NH_3}}{c_{NH_4^+}\, c_{OH^-}}$$

which is usually called the hydrolysis constant of the ammonium ion. For water we have

$$K_A = \frac{c_{OH^-}\, c_{OH_3^+}}{c_{OH_2}} = \frac{K_W}{55.6}$$

where $K_W = c_{OH^-} \cdot c_{OH_3^+}$, the usual dissociation constant of water, and for oxonium ion

$$K_A = \frac{c_{OH_2} \cdot c_{OH_3^+}}{c_{OH_3^+}} = c_{OH_2} = 55.6$$

For a "strong" acid, such as hydrochloric acid, K_A is immeasurably great and for a hydrocarbon it is so small that one would generally say that a hydrocarbon is not an acid at all.

2. Catalysis by Acids and Bases

It is a well-known and striking fact that a considerable number of reactions in aqueous solution can be accelerated by increasing the concentration of hydrogen ion, that of hydroxyl ion or that of either. In most cases that have been carefully studied it is found that the increase in reaction rate is at least approximately proportional to the concentration of hydrogen ion or hydroxyl ion, as the case may be. That is to say, the velocity constant *k* of the reaction is given by

$$k = k_0 + k_{OH_3^+} \cdot c_{OH_3^+} + k_{OH^-} \cdot c_{OH^-}$$

where k_0, $k_{OH_3^+}$ and k_{OH^-} are at each temperature constants for the reaction, while $c_{OH_3^+}$ and c_{OH^-} are the concentrations of hydrogen ion and hydroxyl ion, respectively; any of the constants k_0, $k_{OH_3^+}$ or k_{OH^-} may be negligibly small or zero.

According to our present point of view the hydrogen and hydroxyl ions are not unique as the carriers of acid and basic properties; there is, however, no *a priori* reason to expect that the position they hold as catalysts is unique. On the contrary, one would expect that other acid and basic molecules should act as catalysts as well. The available experimental data do not disagree with this theory of more general acid and basic catalytic effects because in most actual cases the conditions of the experiments have been such that the effects of other catalysts would have been masked by those of OH_3^+ and OH^-. In the few cases where this is not so, "anomalies" in the catalytic actions are detectable[3] for which our present suggestion seems to furnish a reasonable explanation.

This theory has already been verified in this Laboratory for the basic catalysis of the decomposition of nitramide.[4] Dawson and Carter's more recent experiments[5] on the reaction between acetone and iodine also show that this reaction is catalyzed not only by hydroxyl and oxonium ions but also by the anions and undissociated molecules of weak acids. In the solutions used by them, however, the effects of the various catalysts are difficult to separate and we cannot agree with their computations, which involve a confusion between concentration and activity.

The investigations on nitramide have shown that this substance decomposes slowly in aqueous solution at a rate unaffected by neutral salts at small concentration and by strong acids, provided the solution is at least slightly acid, but is decomposed very rapidly in alkaline solution; in other words, the reaction is not affected by oxonium, but is strongly catalyzed by hydroxyl ions. The decomposition has been studied in buffer solutions of the type acetic acid–sodium acetate and also in buffer solutions of the type aniline–anilinium chloride, the solutions being in all cases sufficiently dilute so that the salt effect could be neglected and sufficiently acid so that the effect of hydroxyl could be neglected. Any acceleration observed could thus only be due to the constituents of the buffer. The results obtained showed that there was a pronounced effect proportional to the concentration of the basic constituent of the buffer and independent of the acid constituent. This can be expressed by the formula

$$k = k_0 + k_B c_B$$

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[3] Kuhn and Jacob, *Z. physik. Chem.*, **113**, 389 (1924).

[4] (a) Brönsted and Pedersen, *ibid.*, **108**, 185 (1924); (b) Brönsted and Duus, *ibid.*, **117**, 299 (1925).

[5] Dawson and Carter, *J. Chem. Soc.*, **1926**, 2282.

where c_B is the concentration of the base and k_B a constant characteristic of the base.

Similarly, if a reaction is catalyzed by OH_3^+ we should expect it also to be accelerated by other acids such as the undissociated molecule of formic acid. It should be mentioned that this effect would be that postulated in the so-called "dual theory of catalysis."[6] This theory was put forward owing to a misunderstanding of salt effect, now explained, on the basis of the theory of the complete dissociation of strong electrolytes,[7] and has little in common with our present point of view.

3. The Salt Effect

So far in our discussion we have made no distinction between activity and concentration; in other words we have ignored salt effect, and we must now consider briefly what part it plays in catalysis.

According to the theory of reaction rate in dilute solution,[8] which has now been confirmed experimentally in a number of cases,[9] the velocity of a reaction between X and Y is given in dilute solution by the expression $k\ c_Xc_Yf_Xf_Y/f_{XY}$, where k is a constant for a given solvent and temperature, c_X and c_Y are the concentrations of the reactants, f_X, f_Y and f_{XY} are the activity coefficients of the molecular species X, Y and a complex XY, respectively. The addition of a neutral salt may affect the reaction rate in two ways. First, it may alter the factor f_Xf_Y/f_{XY}; this is termed primary salt effect. Most catalytic reactions fall in the class where one of the reactants, say X, is uncharged, in which case the complex XY has the same charge as Y and so both f_X and f_Y/f_{XY} differ but little from unity; the factor f_Xf_Y/f_{XY} then varies but slightly and linearly with the concentration. Available data show that when only one of the reactants is charged, the primary salt effect is at the most 10% in decimolal solution and is usually much less. Secondly, addition of salt may affect the actual concentration c_X or c_Y of either reactant by causing a shift in an equilibrium involving X or Y; for example, if one of the reactants is hydroxyl ion in a buffer solution the addition of neutral salt may alter its concentration by shifting the buffer equilibrium. This is called secondary salt effect. It is often

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[6] (a) Acree and Johnson, *Am. Chem. J.*, **37**, 410 (1907); (b) *ibid.*, **38**, 258 (1907). (c) Senter, *J. Chem. Soc.*, **91**, 460 (1907). (d) Lapworth, *ibid.*, **97**, 19 (1910). (e) Taylor, *Z. Elektrochem.*, **20**, 201 (1914). (f) Dawson and Powis, *J. Chem. Soc.*, **103**, 2135 (1913). (g) Dawson and Reiman, *ibid.*, **107**, 1426 (1915).

[7] Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).

[8] (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); (b) *ibid.*, **115**, 337 (1925); (c) Bjerrum, *ibid.*, **108**, 82 (1923); (d) *ibid.*, **118**, 251 (1925).

[9] (a) Brönsted and Teeter, *J. Phys. Chem.*, **28**, 579 (1924). (b) Brönsted and Delbanco, *Z. anorg. Chem.*, **144**, 248 (1925). (c) Brönsted and King, THIS JOURNAL, **47**, 2523 (1925). (d) Bray and Livingston, *ibid.*, **45**, 1251 (1923). (e) Livingston and Bray, *ibid.*, **45**, 2048 (1923). (f) Kilpatrick, *ibid.*, **48**, 2091 (1926). (g) Harned, *ibid.*, **49**, 1 (1927). (h) Brönsted and Livingston, *ibid.*, **49**, 435 (1927).

possible, by choosing one's solutions judiciously, to avoid secondary salt effect in studying catalysis and this should for preference be done whenever it is desired to measure the effect of a definite catalyst.

4. The Mutarotation of Glucose

From the standpoint of the present theory the probability of an appreciable catalysis by ordinary acid and basic molecules in aqueous solution involves the presence of a marked effect by OH_3^+ and OH^-. In other words, the reaction to be investigated should be very sensitive to these two ions in order that the effect of weaker acids and bases may be detectable. The mutarotation of glucose fulfils these conditions of sensitiveness.

The rather numerous researches on this reaction have been ably reviewed by Hudson[10] and again by Kuhn and Jacob[3] and therefore need not be considered in detail. It has been established that the process known as the mutarotation of glucose is a balanced one,[11]

$$\alpha\text{-glucose} \rightleftharpoons \beta\text{-glucose}$$

If k_α and k_β are the velocity constants of the two opposed processes, then equilibrium is approached according to the usual exponential law of a unimolecular process with the constant $k_\alpha + k_\beta$ the same from whichever direction the equilibrium state is approached. The constant whose value is always given in the literature is not $k_\alpha + k_\beta$ but $(k_\alpha + k_\beta) \log_{10} e$; to facilitate comparison we shall from now onward also use this constant and denote it by k.

In aqueous solutions k is given at least approximately by a formula of the type[12]

$$k = k_0 + k_{OH_3^+} c_{OH_3^+} + k_{OH^-} c_{OH^-}$$

where $c_{OH_3^+}$ and c_{OH^-} are the concentrations of hydrogen and hydroxyl ion, respectively, while k_0, $k_{OH_3^+}$ and k_{OH^-} depend only on the temperature.

For the temperature 25° Hudson[12] gives the values $k_0 = 0.0096$, $k_{OH_3^+} = 0.258$ and $k_{OH^-} = 9750$, but we shall find that the value for k_{OH^-} is much more uncertain than the other two. Assuming, however, that these values are all of the correct order of magnitude, we see that there is quite a long range of P_H over which k does not differ appreciably from k_0. The actual extent of this range of minimum velocity varies but slightly with the temperature, and between 15 and 30° it is from about $P_H = 4$ to $P_H = 6$.[13] Provided then that apart from OH_2, OH_3^+ and OH^- there are

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[10] Hudson, This Journal, **32**, 889 (1910).

[11] That the mutarotation of sugars is a balanced reaction was first suggested by Lowry, *J. Chem. Soc.*, **75**, 212 (1899). It was verified experimentally for lactose by Hudson, *Z. physik. Chem.*, **44**, 487 (1903) and shortly after for glucose by Lowry, *J. Chem. Soc.*, **83**, 1314 (1903).

[12] Hudson, This Journal, **29**, 1571 (1907).

[13] Nelson and Beegle, *ibid.*, **41**, 559 (1919).

no catalysts present, k_0 is the minimum obtainable value of k. The reaction which is determined by k_0, we shall call the "spontaneous reaction." It is easy to obtain reliable values for k_0 by using water containing a mere trace of acid; water saturated with the carbon dioxide from the air is probably sufficiently acid to give the minimum value of k. Hudson and Dale[14] have collected and compared the values obtained by Hudson and others for k_0 at various temperatures; the agreement with the Arrhenius formula for temperature effect is excellent. The intrapolated value for 18° is 0.0052, while our own experiments give 0.00530.

$k_{OH_3^+}$ is determined most simply by measuring k in solutious of a strong monobasic acid of concentrations up to tenth or twentieth molal; assuming that the acid is completely dissociated, an assumption which for such dilute solutions gives an error certainly much less than the experimental one of 1 or 2%, the concentration of OH_3^+ is simply the stoichiometric concentration of the acid. If k is then plotted against this concentration, a straight line is obtained whose intercept on the k axis is k_0 and whose slope is $k_{OH_3^+}$. Hudson and Dale[14] have in this way determined $k_{OH_3^+}$ at 25 and 30°. By extrapolation according to the Arrhenius formula the value for 18° is 0.13, while Meyer,[15] on the basis of less accurate experiments, finds 0.124 and our own experiments give 0.145. Andrews and Worley[16] in a recent paper state that they have confirmed Hudson's value for $k_{OH_3^+}$ at 25°. Their results are, however, given in terms of an unusual concentration scale and it seems probable that there has been some error in computing the concentrations, for their published data correspond to a value of 0.15 for $k_{OH_3^+}$ as compared with Hudson's value 0.26, while they find the same value, 0.0096, as Hudson for k_0.

From the fact that good straight lines are obtained it follows that primary salt effect is undetectable in these dilute solutions. We have confirmed this in solutions containing, as well as the strong acid, various neutral salts up to an ionic strength of 0.1.

As far as hydrogen-ion catalysis is concerned, Hudson's experiments are still the clearest to interpret, the simplest to compute from and quite as accurate as any later ones. Most modern workers have, however, preferred to define their solutions by using the hydrogen electrode.[3,17] This immediately introduces several unnecessary complications. First, there is the inevitable uncertainty of the liquid-junction e.m.f.; it is under the most favorable conditions doubtful to what extent this can be neglected; Scatchard[18] has shown, moreover, that the presence of sucrose has a marked effect on its value and it is extremely probable that glu-

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[14] Hudson and Dale, THIS JOURNAL, **39**, 320 (1917).

[15] Meyer, *Z. physik. Chem.*, **62**, 68 (1908).

[16] Andrews and Worley, *J. Phys. Chem.*, **31**, 882 (1927).

[17] Euler, Ölander and Rudberg, *Z. anorg. Chem.*, **146**, 45 (1925).

[18] Scatchard, THIS JOURNAL, **48**, 2026 (1926).

cose, if present, will act similarly. Secondly, even if one succeeds in eliminating the liquid-junction e.m.f., the hydrogen electrode measures the activity of the hydrogen ion and not its concentration, which in dilute solutions determines the reaction rate. The situation becomes still more involved when the e.m.f. measurements are performed at a different temperature from that of the reaction velocity measurements, as has been done by Euler.[17] A similar criticism applies to Nelson and Beegle's[13] measurements of hydrogen-ion concentration by a combination of indicator and e.m.f. measurements, as the salt effect on the dissociation equilibrium of the indicator is a complicating factor which cannot be neglected. All these complications are, however, due to an injudicious use of the hydrogen electrode or an indicator in a case where it is much simpler and more accurate to use dilute solutions of a strong monobasic acid and equate the stoichiometric concentration of acid with the hydrogen-ion concentration, as done by Hudson.

As regards the effect of the hydroxyl ion, the situation is very different; the order of magnitude of k_{OH^-} is 10^4 and the reaction is immeasurably fast at a P_{H} greater than 9. It is therefore essential to work in buffer solutions, and we are at once disturbed by numerous difficulties when we try to determine the concentration of hydroxyl ion. Most modern workers have used the hydrogen electrode;[3,17] one is thus faced with all the various complications mentioned before and in addition there is our ignorance of the value of the product $c_{\mathrm{OH}_3^+} \cdot c_{\mathrm{OH}^-}$ in more or less complicated salt solutions. In other words, one has to make assumptions about the activity coefficients of OH_3^+ and OH^- in the buffer solutions; this being so, one might as well assume reasonable values for activity coefficients from the beginning and calculate the hydroxyl-ion concentration directly from the composition of the buffer solution. By this method one introduces no new uncertainties and one does avoid that of the liquid-junction potential. Now most of the data are for buffer solutions containing carbonates, phosphates, citrates or other multivalent ions of which our knowledge of activity coefficients is rather meager. One exception is the experiments of Osaka[19] performed at 25° in solutions containing mixtures of ammonia and ammonium chloride. Now the activity coefficients of HCl, KOH and the various alkaline chlorides, as given by Scatchard,[20] are probably accurate to 1% and at concentrations below 0.07 *M* they all agree to within 4%. We can, therefore, choose values for the activity coefficient of any univalent ion, in solutions containing no ions of higher charge, which are probably accurate to about 2%. The presence of glucose in the solution will presumably alter these values somewhat, but as we know nothing of the magnitude of this effect we must neglect

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[19] Osaka, *Z. physik. Chem.*, **35**, 661 (1900).

[20] Scatchard, This Journal, **47**, 648 (1925).

it; this procedure would still be necessary in order to calculate hydrogen- or hydroxyl-ion concentration even if it were possible to measure hydrogen-ion activity accurately. The following table shows the results obtained from Osaka's experiments. The first two columns give the concentrations of NH_4Cl and NH_3, respectively; the third gives the value assumed for f_1, the activity coefficient of a univalent ion at the corresponding concentration of NH_4Cl. Now from the equilibrium

TABLE I

OSAKA'S EXPERIMENTS WITH AMMONIA-AMMONIUM ION BUFFER SOLUTIONS ($t = 25°$)

$c_{NH_4Cl} \times 10^2$	$c_{NH_3} \times 10^3$	f_1	$\frac{K_{NH_3}}{f_1^2} \times 10^5$	$c_{OH^-} \times 10^6$	$k \times 10^2$	$(k - k_0) \times 10^2$	$\frac{k - k_0}{c_{OH^-}} \times 10^{-4}$
6.67	4.42	0.80	2.83	1.87	3.60	2.64	1.41
5.00	3.32	.815	2.72	1.81	3.35	2.39	1.32
2.25	2.14	.865	2.42	2.30	3.26	2.30	1.00
2.25	3.22	.865	2.42	3.46	3.82	2.86	0.83
3.33	4.42	.845	2.54	3.37	4.46	3.50	1.04
2.25	4.27	.865	2.42	4.59	4.94	3.98	0.87
2.25	5.35	.865	2.42	5.75	6.40	5.44	0.95
2.25	6.41	.865	2.42	6.90	7.05	6.09	0.87

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + OH_2$$

we have

$$c_{OH^-} = \frac{c_{NH_3}}{c_{NH_4^+}} \frac{K_{NH_3}}{f_1^2}$$

where K_{NH_3} is the dissociation constant of NH_3 at zero salt concentration. The value assumed for K_{NH_3} at 25° is 1.81×10^{-5}.[21] The fourth column gives values of K_{NH_3}/f_1^2 and the fifth those of c_{OH^-} calculated from this equation. The sixth column gives the values observed for k. If we assume that in these solutions the hydroxyl ion is the only cause of the variation in the velocity constant we should have an equation of the form

$$k = k_0 + k_{OH^-}c_{OH^-}$$

The value 0.0096 for k_0 at 25° found by Hudson[12] has been confirmed recently by the very careful experiments of Worley and Andrews.[22] In the seventh column are given values of $(k - k_0)/c_{OH^-}$ or k_{OH^-} calculated from this value of k_0. A glance at these values shows that there is an uncertainty of 50% in the value 9750 for k_{OH^-} computed by Hudson from the same data. It is noticeable that the two values of $(k - k_0)/c_{OH^-}$ that differ markedly from the remainder correspond to solutions of markedly higher salt concentration; it should, therefore, be emphasized that if we had not introduced the factor $1/f_1^2$ to account for secondary salt effect, the deviations in these cases would have been over 12% greater than they appear now. After discussing the results of our own experiments, we shall reconsider these deviations in the light of a possible catalytic effect of the NH_3 molecule.

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[21] Noyes and Kanolt, Carnegie Inst. Wash. Pub., **63**, 285 (1907).

[22] Worley and Andrews, *J. Phys. Chem.*, **31**, 742 (1927).

It has been established that the same unimolecular constant is obtained for the mutarotation of glucose whether the progress of the reaction be measured by the optical rotation, the usual method, or by the refractive index or by the volume of the solution.[23] There is, moreover, little to choose between the three methods as far as accuracy is concerned.

5. Experimental Method and Method of Calculation

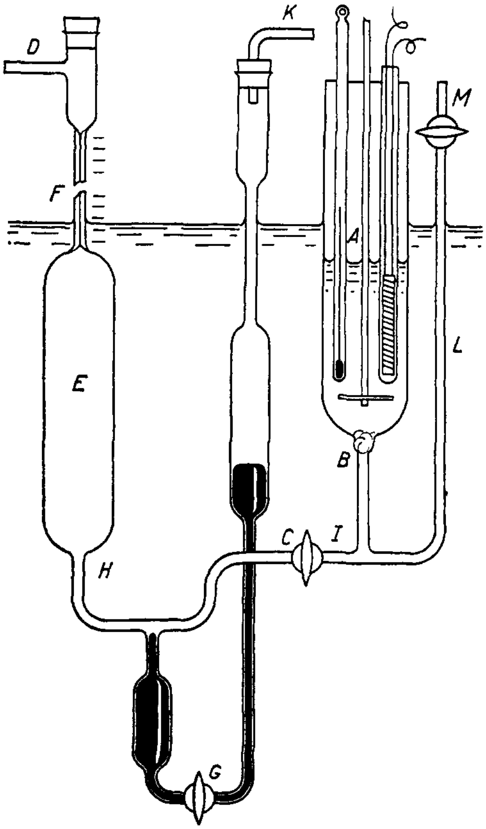

Fig. 1.

The method used by us was the dilatometric. The apparatus is shown in Figure 1. A is the mixing chamber fitted with a mechanical stirrer, a thermometer graduated in fiftieths of a degree centigrade and a quartz-platinum resistance thermometer used as a heating coil. At B was placed a plug of cotton wool. All three stopcocks being closed, the solution was placed in the mixing chamber and stirred; after it had attained the temperature of the thermostat, the thermometer reading was noted. The solution was then heated through rather more than 1° by means of the heating coil and the glucose (18 g. to 180 cc. of solution) was dropped in. It dissolved very rapidly and the temperature fell slightly below its original value. By carefully switching the current on and off it was possible to get the solution to its initial temperature correct to 0.01° within two minutes of dropping in the glucose. The stirrer, thermometer and heating coil were removed and A was closed with a rubber stopper through which passed a glass tube connected to a water pump. Suction was applied for about one minute to remove air bubbles. The stopcock C was then opened and by evacuating through D the solution was drawn up into the dilatometer E as far as the top of the capillary F when C was closed. The stopcock G was then opened so that the mercury filling that part of the apparatus shaded in the diagram rose to H; the stopcock C was opened again so that mercury flowed up through C as far as I, when C was quickly closed. Finally, a slight suction was applied to K so as to bring the surface of the solution to a convenient level in the capillary F, and G was closed. The whole operation from the time the glucose was added took about seven minutes. The progress of the reaction was then followed by watching

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[23] (a) Pratolongo, *Rend. ist. lombardo Sci.*, (2), **45**, 961 (1912); (b) Riiber, *Ber.*, **55**, 3132 (1922); (c) **56**, 2185 (1923); (d) **57**, 1599 (1924).

the rise of the meniscus in the capillary; readings were taken with a magnifying glass viewed through a horizontal tube about 5 cm. in length so as to reduce the parallax. The capillary was graduated in millimeters and readings were recorded to 0.05 mm., the error probably being less than 0.1 mm. The graduation of the capillary was calibrated by noting the apparent length of a weighed thread of mercury at different places. It was found that the cross section of the capillary was about 0.60 mm. The scale graduations were uniform with an accuracy of ±1% throughout, but over a range of 70 mm. they were uniform with an accuracy of ±0.25% and only this part of the capillary was used.

Since the change in volume in this reaction is exceptionally small, it was of the greatest importance that there should be no leakage during a reaction. In a number of preliminary experiments in different apparatus, in which mercury was not used to confine the solution, it was found very difficult to keep the tap corresponding to C tight. Although this tap was freshly greased before each experiment, small leaks of the order of a cubic millimeter in several hours were apt to develop. When, however, the solution was confined in the dilatometer by the mercury column it was possible to make five to ten experiments before any leak was detectable and it became necessary to regrease C. The tightness of the stopcock C was easily tested before and after an experiment by applying strong suction to A and watching the meniscus of the liquid in F. An experiment was always rejected if a leak, however slight, was detected. In the reaction diacetone alcohol ⟶ acetone, also studied in a dilatometer first by Koelichen[24] and recently by Åkerlöf[25] such small leaks as those described above would be of no significance. The apparatus was emptied by opening the stopcock M and sucking the solution through L. The capillary F of the dilatometer was cleaned with chromic acid after each experiment except the early ones. One cc. of chromic acid was allowed to trickle through F into E filled with distilled water and became so diluted that it did not attack the grease on the tap C.

The whole apparatus was in a thermostat at 18.0°, the regulation of which was similar to that previously used and described by Brönsted and La Mer.[26] The reading of the thermometer in the bath did not vary over several days more than 0.005°; the temperature of the solution in the dilatometer would certainly fluctuate less than this owing to the insulating property of the glass wall of the dilatometer. The volume of the dilatometer was 165 cc. and the cross-sectional area of the capillary 0.60 sq. mm. The coefficient of expansion of water at 18° is 0.0002 cc. per °C. The observed fluctuations of the height of the meniscus were generally less than 0.1 mm. This corresponds to a temperature fluctuation of $(0.1 \times 0.60)/(165 \times 1000 \times 0.0002) = 0.002°$, that is, a little less than half the fluctuation of the bath itself. Åkerlöf[25] gives a similar calculation for his dilatometer, whose dimensions were not very different from those of ours, and finds that a fluctuation of 0.1 mm. corresponds to a temperature variation of only 0.00003°, but he takes the coefficient of expansion of his aqueous salt solutions to be 0.006 per °C., which must be a mistake. If he observed fluctuations in height of the order of magnitude to be expected from his calculation of temperature effect, they must have been due to some other cause; they would not, however, affect the accuracy of his results, as the volume change of the reaction is so great. In our experiments the volume change calculated according to Riiber's[23] data was about 22 cc. mm., corresponding to a rise of 37 mm., of which about 4 mm. would correspond to the change already taken place in the seven minutes required to fill the dilatometer. The readings in the first ten minutes almost invariably seemed to be too low; this is believed to be due to a trace of water trickling down the wall of the capillary.

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[24] Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).

[25] Åkerlöf, THIS JOURNAL, **48**, 3046 (1926).

[26] Brönsted and La Mer, *ibid.*, **46**, 555 (1924).

The method used for computing the velocity constant was that described by Guggenheim,[27] which avoids the unnecessarily large error of the usual formula owing to the great weight given to the end value, whose accuracy is often less than that of the other individual readings. A series of readings V is made at times t spread over an interval two or three times the length of the period of half-completion of the reaction. A second series of readings V' is then made, each at a time $t + \tau$ exactly a constant interval τ after the corresponding reading V, the interval τ being at least two to three times the period of half-completion. If $\log_{10} (V' - V)$ is then plotted against t, a straight line is obtained whose slope is $-k$. The half-time periods of our reactions were generally 30 to 50 minutes, and the period chosen for t was usually 120 minutes. This

TABLE IIA

TYPICAL EXPERIMENT

Experiment 15.21. Sodium *o*-toluate, 0.075 M. *o*-Toluic acid, 0.0026 M. $k = 6.16 \times 10^{-3}$ min.$^{-1}$.

Time, t Min.	Sec.	Reading (τ = 120 min.) V	V'	$V' - V$	$\log_{10}$ $(V' - V)$	$V' - V$ calcd.	Deviation
0	0	4.395	6.50	2.105	0.323	2.105	0.00
2	0	4.475	6.52	2.045	.311	2.04	+ .005
4	0	4.545	6.535	1.99	.299	1.99	.00
6	0	4.615	6.545	1.93	.286	1.93	.00
8	0	4.695	6.565	1.87	.272	1.875	− .005
10	0	4.76	6.575	1.815	.259	1.82	− .005
12	30	4.83	6.59	1.76	.246	1.76	.00
15	0	4.91	6.60	1.69	.228	1.69	.00
18	0	5.00	6.615	1.615	.208	1.625	− .01
21	0	5.09	6.63	1.54	.187	1.555	− .015
24	0	5.17	6.64	1.47	.167	1.49	− .02
28	0	5.27	6.66	1.39	.143	1.41	− .02
32	0	5.37	6.685	1.315	.119	1.33	− .015
36	0	5.45	6.70	1.25	.097	1.26	− .01
40	0	5.53	6.72	1.19	.076	1.19	.00
45	0	5.64	6.735	1.095	.039	1.105	− .01
50	0	5.72	6.76	1.04	.017	1.035	+ .005
55	0	5.805	6.775	0.97	$\bar{1}.987$	0.96	+ .01
60	0	5.89	6.79	.90	$\bar{1}.954$	.895	+ .005
65	0	5.96	6.795	.835	$\bar{1}.922$	.835	.00
70	0	6.02	6.805	.785	$\bar{1}.895$	.775	+ .01
76	0	6.105	6.82	.715	$\bar{1}.854$	.715	.00
82	0	6.18	6.835	.655	$\bar{1}.816$	.655	.00
88	0	6.235	6.85	.615	$\bar{1}.789$	.60	+ .015
95	0	6.31	6.87	.56	$\bar{1}.748$	.545	+ .015
102	0	6.38	6.88	.50	$\bar{1}.699$	.495	+ .005
110	0	6.44	6.89	.45	$\bar{1}.653$	.45	.00
115	0	6.485	6.895	.41	$\bar{1}.613$	.41	.00

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[27] Guggenheim, *Phil. Mag.*, **1**, 538 (1926).

Table IIB

Typical Experiment

Experiment 15.11. Sodium *o*-toluate, 0.050 *M*. *o*-Toluic acid, 0.0027 *M*. $k = 5.92 \times 10^{-3}$ min.$^{-1}$.

Time, t Min.	Sec.	Reading (τ = 120 min.) V	V'	$V' - V$	$\log_{10}$ $(V' - V)$	$V' - V$ calcd.	Deviation
4	0	4.66	6.585	1.925	0.2845	1.915	+0.01
8	0	4.79	6.60	1.81	.258	1.81	.00
11	0	4.88	6.62	1.74	.241	1.74	.00
14	0	4.97	6.645	1.675	.224	1.675	.00
17	0	5.055	6.655	1.60	.204	1.60	.00
20	0	5.135	6.68	1.545	.189	1.54	+ .005
24	0	5.235	6.695	1.46	.164	1.46	.00
28	0	5.33	6.70	1.37	.137	1.375	− .005
32	0	5.425	6.725	1.30	.114	1.305	− .005
36	0	5.50	6.74	1.24	.093	1.24	.00
40	15	5.595	6.765	1.17	.068	1.17	.00
44	0	5.675	6.78	1.105	.043	1.11	− .005
48	30	5.75	6.79	1.04	.017	1.04	.00
53	30	5.84	6.81	0.97	$\bar{1}.987$	0.975	− .005
59	0	5.92	6.825	.905	$\bar{1}.957$	.905	.00
65	0	6.005	6.84	.835	$\bar{1}.922$	.835	.00
71	0	6.09	6.86	.77	$\bar{1}.887$	.765	+ .005
78	0	6.185	6.88	.695	$\bar{1}.842$	.695	.00
85	0	6.26	6.89	.63	$\bar{1}.799$	.635	− .005
93	0	6.33	6.91	.58	$\bar{1}.763$	.57	+ .01
102	0	6.415	6.92	.505	$\bar{1}.703$	.505	.00

method of computation was checked in a few experiments by using two different values for τ, and the results of the two computations always agreed to within 0.5% with each other and with that obtained by the usual formula, if one assumed a suitable value for the final reading agreeing within the experimental error of 0.1 mm. with both the observed end value and with the end-value obtained by extrapolation. An example of this test is given in the original paper describing the method.

We give in tabular form the complete data for two experiments. The first column gives the times t in minutes and seconds; the second column gives the readings V at the times t; the third gives the readings V' at times $t + \tau$ where τ is 120 minutes; the fourth gives the values of $\log_{10} (V' - V)$; when these are plotted against t the best straight line passes through points corresponding to the values of $(V' - V)$ given in the sixth column. The last column gives the differences between the figures in the fourth and sixth columns; these differences measure the accuracy of the individual readings. In the first example the deviations were unusually great, whereas in the second experiment they were somewhat less than average.

The glucose used was Merck's best anhydrous α-glucose. Two different preparations were made, and a few experiments performed in duplicate with the two samples gave identical results. Rough tests with indicators showed the distilled water used, which was presumably saturated with carbon dioxide from the air, to have a *P*H between 5 and 6 and this was not appreciably altered by dissolving the glucose. Any trace of acid or alkali in the glucose would be negligible, as almost all the experiments, except those to determine the effect of hydrogen ion, were performed in buffer solutions with a *P*H between 4 and 6, the range in which the effects of both hydrogen ion and hydroxyl ion are quite negligible; whenever the buffer solution contained a quantity of weak acid small compared with that of the corresponding salt, the amount of weak acid was checked by titration against very dilute sodium hydroxide, using phenolphthalein as indicator. For the same reason a trace of acid or alkali in the various preparations of weak acids and salts used would be negligible. Whenever there was any possible doubt about the *P*H of the solution being within the range 4 to 6 it was tested colorimetrically.

It has been emphasized by Lowry[28] that one can never be certain that there is not present some minute trace of an unknown catalyst. But, whatever precautions one took to purify one's material, one could never be sure that this hypothetical catalyst was removed, as long as its nature or even existence was quite unknown. We were therefore satisfied with assuring ourselves that none of the materials used contained as impurity an appreciable quantity of any substance known to be a catalyst. As, however, the velocity constant for a given experiment appeared to be quite definite with an accuracy of 0.5%, as shown by the agreement between two independent computations using different values for the time interval τ, whereas the disagreement between individual experiments was occasionally over 2%, it is just possible that there was sometimes present a trace of such an obscure catalyst whose amount could not be controlled. It is also possible that there may have been some surface reaction at the glass wall varying with the state of the glass; but the regularity of our results indicate that any effects of this type must have been small, not greater than 2%. The only experiments, other than some of the earliest ones, that seem to show irregularities greater than 2% are those in solutions of a strong acid; this may conceivably have been due to some reaction of the acid with the glass. Partly through lack of time, but especially because our main object was to study the effect of catalysts other than hydrogen ion, we did not investigate the cause of the smaller accuracy of the experiments with a strong acid.

For each experiment 200 cc. of solution was made up to a definite concentration in gram molecules per liter. Of this, 180 cc. was used for the experiment, together with 18 g. of glucose; the remaining 20 cc. of solution was used for checking its *P*H.

[28] Lowry, *J. Chem. Soc.*, **127**, 1371 (1925).

6. The "Spontaneous" Reaction and the Hydrogen-Ion Catalysis

Table III gives the results of experiments to determine k_0, in which experiments the solutions contained, apart from water, no acid or base. The table shows that the value $(5.30 \pm 0.10) \times 10^{-3}$ min.$^{-1}$ obtained for k was reproducible at various times over a period of one and a half years, was the same for both preparations of α-glucose and was unaffected by salts up to an ionic strength of 0.2, even with salts containing bivalent and tervalent ions. We therefore consider ourselves justified in refusing to admit the possibility of a neutral salt effect greater than 2% in the dilute solutions used in all our experiments.

TABLE III

EXPERIMENTS TO DETERMINE k_0 AND SHOW ABSENCE OF NEUTRAL SALT EFFECT (t = 18°)

Date	Glucose prepn.	Concn. of acid	Concn. neut. salt, moles per liter	$k \times 10^3$ min.$^{-1}$
19-12-25	I	$HClO_4$ 1.0×10^{-4}		5.20
13-1-26	I	HCl 1.0×10^{-5}		5.23
14-1-26	I	HCl 1.0×10^{-4}		5.31
19-1-26	I	$HClO_4$ 1.0×10^{-4}	NaCl .100	5.25
20-1-26	I	$HClO_4$ 1.0×10^{-4}	KNO_3 .200	5.18
13-9-26	I	HCl 1.0×10^{-4}		5.29
29-9-26	I	$HClO_4$ 1.0×10^{-4}	NaCl .200	5.24
12-10-26	I	$HClO_4$ 1.0×10^{-4}	KNO_3 .100	5.36
14-10-26	I	$HClO_4$ 1.0×10^{-4}	KNO_3 .100	5.40
15-10-26	I	$HClO_4$ 1.0×10^{-4}	KNO_3 .200	5.28
20-10-26	II	$HClO_4$ 1.0×10^{-4}		5.27
21-10-26	II	$HClO_4$ 1.0×10^{-4}		5.27
26-10-26	I	$HClO_4$ 1.0×10^{-4}	$Ba(NO_3)_2$ .05	5.43
27-10-26	I	$HClO_4$ 1.0×10^{-4}	$Ba(NO_3)_2$ .025	5.30
6-4-27	II	$HClO_4$ 1.0×10^{-4}	$[Co(NH_3)_6](NO_3)_3$ .040	5.36
6-7-27	II	Distilled water[a]		5.42

[a] If the water were saturated with carbon dioxide from the air the effect of hydroxyl ion would almost certainly be negligible. As, however, most of the carbon dioxide is probably sucked out before the solution is brought into the dilatometer, the P_H of the solution may have been just over 6; this would be sufficient to account for the slightly high value of the reaction rate constant in the experiment with distilled water as solvent.

Table IV gives the results of experiments with perchloric acid solutions to determine the effect of oxonium ion. The results are also shown plotted in Fig. 2, from which the value 0.145 was obtained for $k_{OH_3^+}$. The last column of the table gives values of $k \times 10^3$ calculated from the formula

$$k = 0.00530 + 0.145\, c_{OH_3^+}$$

where $c_{OH_3^+}$ is the concentration of hydrogen ion reckoned as equal to the stoichiometric concentration of perchloric acid. As mentioned above this set of experiments is less concordant than any other set, the error of individual experiments being in some cases 3 or 4%. The results are,

TABLE IV

EXPERIMENTS TO DETERMINE THE EFFECT OF OXONIUM ION (t = 18°)

Date	Glucose prepn.	Concn. of $HClO_4$ $\times 10^2$	Concn. neut. salt, moles per liter	$k \times 10^3$, obs.	$k \times 10^3$, calcd.
15-1-26	I	0.10		5.42	5.44
16-1-26	I	0.99		6.67	6.73
18-1-26	I	2.00		8.00	8.20
19-1-26	I	3.00		9.37	9.65
21-1-26	I	4.00		11.26	11.10
25-1-26	I	3.25	KNO_2.20	10.02	10.01
26-1-26	I	1.00	KNO_3.20	6.51	6.75
22-9-26	I	0.96		6.87	6.67
23-9-26	I	1.92		8.28	8.04
25-9-26	I	2.89		9.50	9.41
26-9-26	I	3.85		10.80	10.88
28-9-26	I	4.33		11.38	11.59
11-10-26	I	0.48		6.02	6.00
16-10-26	II	0.48		6.00	6.00
25-10-26	II	2.47		8.92	8.88
8-6-27	II	2.50	NaCl.20	8.89	8.92
9-6-27	II	2.00	$Ba(NO_3)_2$.050	8.21	8.20

however, sufficient to show that the effect of oxonium ion is proportional to its concentration and that primary salt effect is undetectable.

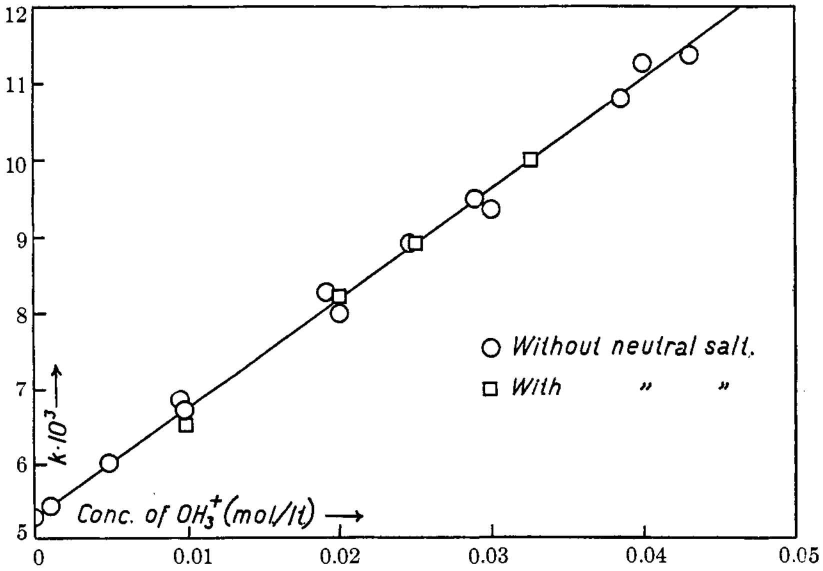


Fig. 2.—Catalysis by hydrogen ions.

Kuhn and Jacob[3] claim to have shown that the effect of strong acid is proportional not to the hydrogen-ion concentration but to the hydrogen-ion activity; but their experiments are not sufficiently accurate to distinguish between activity and concentration in the absence of neutral salt, while those in molar solutions of neutral salt are simply explained by a linear salt effect of the order 10% for a molar solution, which is no more than is to be expected.

TABLE V

EXPERIMENTS TO DETERMINE THE EFFECT OF BASIC ANIONS (t = 18°)

Concn., sodium salt	Concn., acid	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
	Acetate		
0.020	0.020	5.90	5.88
.025	.025	6.02	6.02
.025	.050	6.00	*[a]6.08
.030	.070	6.37	*6.26
.040	.060	6.63	*6.50
.050	.050	6.83	6.75
.065	.085	7.33	*7.23
.065	.060	7.43	*7.17
.075	.075	7.38	7.47
.090	.110	7.96	*7.95
.100	.100	8.24	8.19
.100	.100	8.22	8.19
.110	.090	8.57	*8.43
.125	.125	8.83	*8.79
.125	.124	8.91	8.91
.200	.198	10.96	11.08
	Propionate		
0.010	0.010	5.65	5.60
.030	.070	6.27	*6.29
.040	.020	6.58	6.47
.040	.020	6.53	6.47
.040	.060	6.60	*6.55
.050	.050	6.81	*6.81
.060	.065	7.13	*7.12
.075	.075	7.57	*7.57
.100	.100	7.97	*8.32
.100	.100	8.21	8.32
.110	.115	8.60	*8.63
.125	.125	9.15	9.08
.150	.150	9.85	9.83
	Benzoate		
0.040	0.010	5.98	*5.91
.070	.010	6.46	*6.36
.075	.010	6.53	6.44
.090	.020	6.56	*6.67
.100	.020	6.72	6.82
.110	.020	6.83	*6.97
.125	.020	7.12	7.20
.150	.020	7.58	7.58

TABLE V (*Continued*)

Concn., sodium salt	Concn., acid	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
	Formate		
0.040	0.005	6.00	*5.99
.050	.003	6.19	*6.14
.060	.005	6.23	*6.31
.060	.019	6.44	*6.40
.075	.004	6.53	*6.56
.100	.005	6.92	*6.97
.100	.005	7.12	6.97
.125	.006	7.25	*7.39
.125	.005	7.48	7.39
.150	.007	7.78	7.80
.200	.009	8.48	8.44
.250	.014	9.43	9.49
	Salicylate		
0.050	0.001	5.45	5.53
.050	.001	5.50	5.53
.075	.001	5.68	5.65
.100	.001	5.77	5.76
	Glycolate		
0.050	0.005	6.01	5.96
.075	.005	6.41	6.36
.100	.010	6.75	6.73
.125	.010	7.09	7.07
	Chloro-acetate		
0.050	0.0007	5.51	5.57
.075	.0007	5.66	5.70
.100	.001	5.88	5.84
	Trimethylacetate		
0.011	0.010	5.63	5.64
.0255	.0245	6.20	6.11
.030	.030	6.21	6.24
.051	.049	6.84	6.91
.0765	.0735	7.66	7.70
	Phenylacetate		
0.025	0.006	5.82	5.82
.050	.011	6.44	6.33
.075	.009	6.90	6.83
.100	.009	7.32	7.33
.150	.030	8.41	8.38
	o-Toluate		
0.050	0.003	5.92	5.91
.075	.003	6.16	6.21
.100	.005	6.50	6.52
.125	.006	6.84	6.83

Table V (*Concluded*)

Concn., sodium salt	Concn., acid	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
	Mandelate		
0.050	0.001	5.80	5.84
.100	.001	6.38	6.38
.125	.001	6.66	6.65
	Cyanacetate		
0.100	0.001	5.66	5.68
.125	.001	5.78	5.78
	o-Chlorobenzoate		
0.050	0.001	5.60	5.62
.075	.001	5.74	5.78
.100	.001	5.94	5.94

[a] The experiments marked * were carried out at a considerably earlier period than the similar ones not so marked and in some cases are rather below average accuracy, especially when the reaction rate is high.

7. The Effect of Monobasic Acids and their Anions

In Table V the first three columns give the results of experiments performed to determine the catalytic effect of the anions of weak monobasic acids. All the solutions were made up in such a way that the *P*H was between 4 and 6; there could therefore be no appreciable catalysis by either hydrogen or hydroxyl ion. As we have already shown that neutral salt effect is certainly not more than 2%, it follows that any considerable increase in the velocity constant can only be due either to the anions, acting as bases, or to the undissociated molecules of the acid. In Figs. 3A, 3B and 3C the values of k are plotted against the concentration of

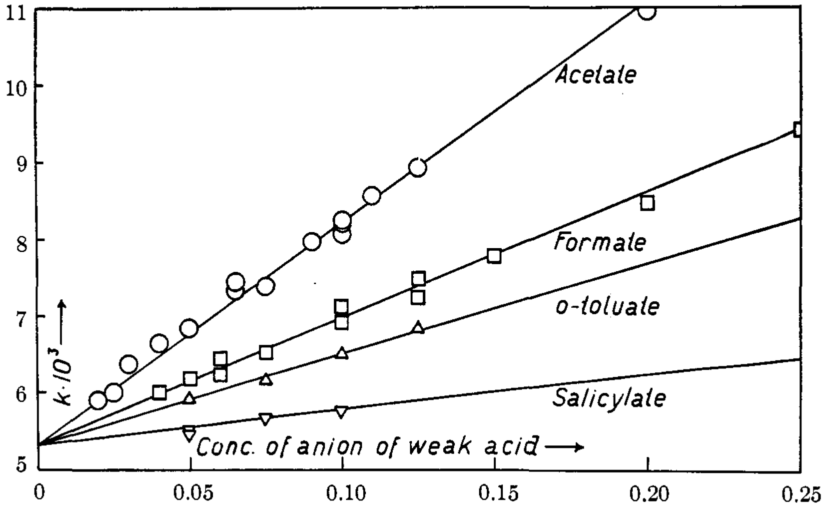


Fig. 3A.—Catalysis by anions.

the anion. They leave no doubt that the anions are catalytically active in proportion to their concentration. In the case of the strongest bases trimethylacetate, propionate and acetate ions the effect is over one-fifth that of oxonium ion; even cyanacetate ion, the weakest base of this type studied, has an effect about one-fortieth that of oxonium.

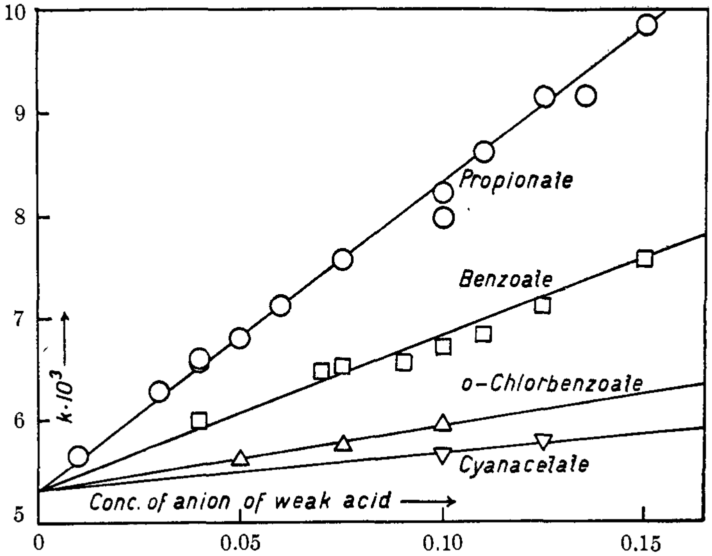


Fig. 3B.—Catalysis by anions.

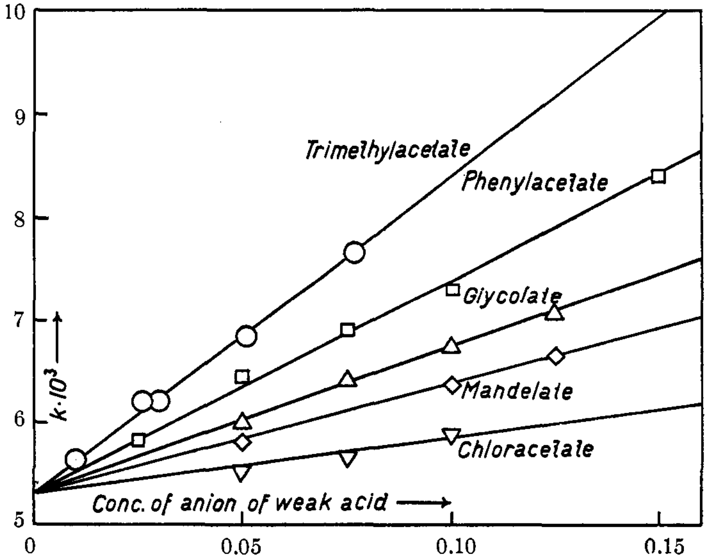


Fig. 3C.—Catalysis by anions.

In the first four columns of Table (VI) are given the results of experiments to determine the effect, if any, of the undissociated acid molecules. The method was to make a series of experiments with a constant concentration of the sodium salt, that is, of anion, and various concentrations of the acid, so far as possible keeping the P_H above 4; this was not always possible and in a number of cases the effect of oxonium is not quite negligible; the concentration of hydrogen ion can, however, be calculated approximately from the composition of the buffer solution, using rough values

Table VI

Experiments to Determine the Effect of Undissociated Acid Molecules

(t = 18°)

Concn., sodium salt	Concn., acid	Concn., hydrogen ion $\times 10^4$	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
		Formic Acid		
0.100	0.005	0.1	6.92	6.97
.100	.025	1	7.06	7.06
.100	.050	1	7.24	7.18
.100	.100	3	7.38	7.41
.100	.150	4	7.63	7.64
.125	.005	0.1	7.48	7.39
.125	.006	.1	7.25	7.39
.125	.124	3	7.86	7.93
.125	.250	6	8.50	8.52
		Glycolic Acid		
0.100	0.010	0.2	6.75	6.73
.100	.025	1	6.81	6.81
.100	.075	2	7.04	7.09
.100	.100	2	7.26	7.23
		Mandelic Acid		
0.100	0.001	0.1	6.38	6.38
.100	.025	2	6.58	6.55
.100	.050	4	6.70	6.71
.100	.100	7	7.04	7.05
		Acetic Acid		
0.020	0.020	0.3	5.90	5.88
.020	.105	2	6.10	6.13
.020	.199	3	6.32	6.36
		Trimethylacetic Acid		
0.010	0.010	0.2	5.65	5.64
.010	.100	2	5.88	5.84
.0255	.0245	0.2	6.20	6.11
.0255	.100	1	6.26	6.31
.0255	.100	1	6.31	6.31
		Phenylacetic Acid		
0.025	0.006	0.2	5.82	5.82
.025	.074	2	5.98	6.03

TABLE VI (*Concluded*)

Concn., sodium salt	Concn., acid	Concn., hydrogen ion $\times 10^4$	$k \times 10^3$ obs.	$k \times 10^3$ calcd.
		Propionic Acid		
0.040	0.020	0.1	6.53	6.47
.040	.020	.1	6.58	6.47
.040	.060	.2	6.60	6.55
.040	.110	.6	6.76	6.66
.040	.160	1	6.77	6.82
		Chloro-acetic Acid		
0.100	0.001	0.2	5.88	5.84
.100	.025	6	6.09	6.10
.100	.050	12	6.35	6.35
.100	.075	18	6.62	6.61

for activity coefficients, and the values computed are given in the third column. As we have found $k_{OH_3^+}$ to be 0.145, a hydrogen-ion concentration of 7×10^{-4} gives a catalytic effect of only 0.10×10^{-3} min.$^{-1}$ so that the correction to be applied for the oxonium catalysis is never more than 2% except in the experiments with chloro-acetic acid.

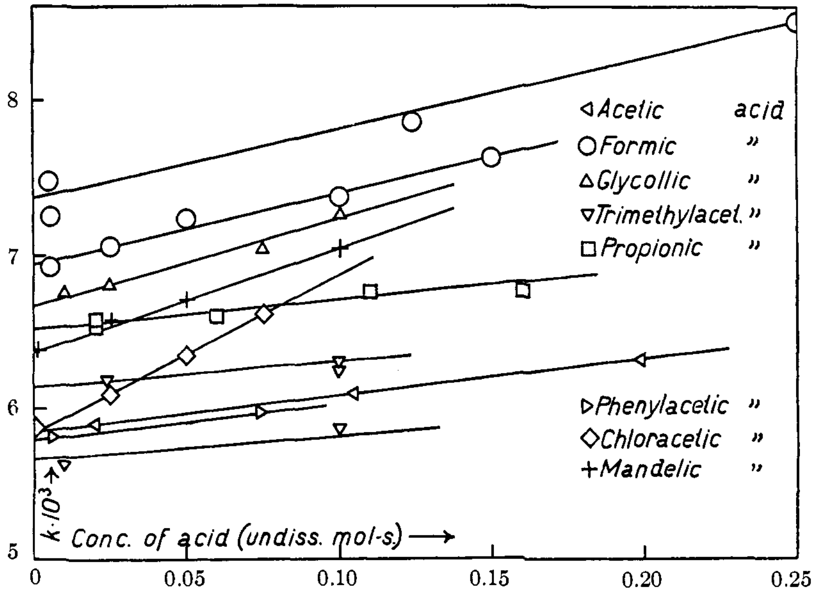


Fig. 4.—Catalysis by anions and undissociated acids.

In Fig. 4 the values of k for each series of constant concentration of sodium salt are plotted against the concentration of acid. The slopes of the straight lines obtained give the values of k_A, the catalytic constants of the various acid molecules, except for the above-mentioned correction for OH_3^+ catalysis. When two sets of experiments have been made with the same acid, the constant concentration of salt in each set being different in the two cases, two parallel straight lines are obtained; the different intercepts on the k axis correspond to the different concentrations of the catalytic anion. Each straight line as drawn has been made to pass through a point corresponding to a point on the lines in Figs. 3A, 3B, 3C; in other words, the computations of the acid and basic catalytic constants are not independent of each other. The catalytic effect of the undissociated acid molecule seems to be so small in the case of the weakest acids that the existence of any effect might be disputed, but the effect of the formic acid, glycolic acid and mandelic acid molecules is unquestionable. In the case of chloro-acetic acid the hydrogen-ion catalysis, though important, cannot account for more than one-third of the increase in the velocity constant with increasing concentration of acid. With a still stronger acid, such as cyanacetic acid, unless one used a high concentration of the salt, the hydrogen-ion catalysis would always be greater than that of the acid molecules. There is thus in this reaction a real difficulty in detecting this catalysis by undissociated acid molecules; if the acid is too weak the effect is too small to observe; if the acid is too strong the effect is masked by that of oxonium ion and most common acids of suitable strength are insufficiently soluble. The same difficulty may have obscured such an acid catalysis in other reactions where the whole effect has been ascribed to OH_3^+. Our main evidence for catalysis by the "undissociated" acid molecules must rest on the experiments with formic acid, glycolic acid and mandelic acid; the results obtained with the weaker acids and with chloro-acetic acid, though not convincing by themselves, lend additional support.

TABLE VII

CATALYTIC CONSTANTS OF UNIVALENT NEGATIVE BASES AND UNCHARGED ACIDS

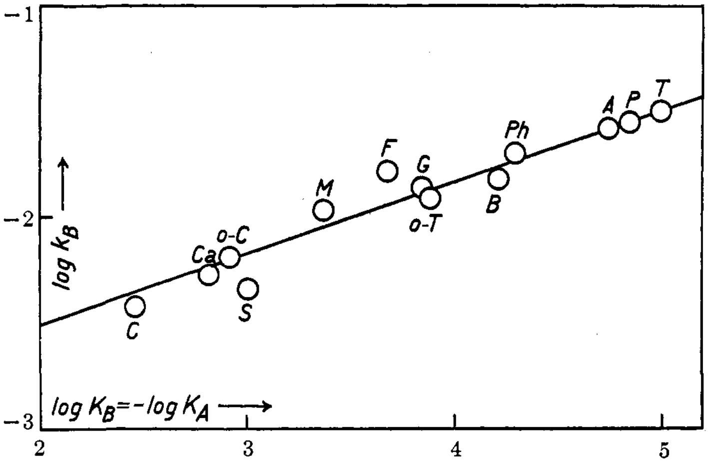
(t = 18°)

Acid	Acid (dissoc.) const. $K_A \times 10^4$	Acid catalytic const. $k_A \times 10^3$	Basic catalytic const. $k_B \times 10^3$	$k_B \times 10^3$ theoret.
Trimethylacetic	0.10	2.0	31.4	31.5
Propionic	.14	2.1	28.1	28
Acetic	.18	2.4	26.5	26.5
Phenylacetic	.5	2.8	20.0	18
Benzoic	.6	...	15.2	17
o-Toluic	1.3	...	12.2	13
Glycolic	1.4	5.6	13.7	13
Formic	2.1	4.6	16.5	11
Mandelic	4.3	5.7	10.8	8
Salicylic	10	...	4.6	6.5
o-Chlorobenzoic	13	...	6.4	6.5
Chloro-acetic	15	6.8	5.4	5.5
Cyanacetic	35	...	3.8	4

The important question of how the acid and basic catalysis depends upon the strength of the acid or base is answered by the figures in Table VII. Here are given the catalytic constants k_A and k_B calculated from the data of Tables V and VI; the figures in the last column will be explained later. The acids are arranged in order of increasing acid (dissociation) constant K_A. The third column gives k_A the constant for acid catalysis by the "undissociated" molecules and the fourth gives k_B, the constant for the basic catalysis by the anions. The last columns of Tables V and VI give values for k calculated from the formula

$$k = 0.00530 + 0.145\, c_{OH_3^+} + k_B c_B + k_A c_A$$

where k_B and k_A have the values given in Table VII, c_B and c_A are the concentration of anion (base) and undissociated molecule (acid), respectively.



T, trimethylacetate; Ph, phenylacetate; G, glycolate; S, salicylate; C, cyanacetate; P, propionate; B, benzoate; F, formate; *o*-C, *o*-chlorobenzoate; A, acetate; *o*-T, *o*-toluate; M, mandelate; Ca, chloro-acetate.

Fig. 5.—Dependence of basic catalysis on the strength of the basic anion.

In the experiments of Table V the second term is always quite negligible and the last either negligible or small so that the formula becomes approximately

$$k = 0.00530 + k_B c_B$$

In the data of Table VI the second term is never greater than 0.00010 except in the experiments with chloro-acetic acid and the third term is constant for each series.

Brönsted and Pedersen[4a] found a very simple relation between k_B, the catalytic constant of an anion in the decomposition of nitramide, and K_B, the basic constant of the anion, which by definition is the reciprocal of K_A, the dissociation constant of the conjugate acid. The relation was

$$k_B = 6.2 \times 10^{-5}\, K_B^{0.83}$$

so that plotting log k_B against log K_B they obtained a straight line of slope 0.83. In Fig. 5 we have plotted the results for the anion basic catalysis of the mutatoration of glucose in a similar way. In this case we also obtain an approximate straight line, but the slope is 0.34 and the relation between k_B and K_B is less exact than for the nitramide catalysis. The last column of Table VII gives values of k_B corresponding to the straight line in Fig. 5. These values agree with the observed values in most cases within 2×10^{-3} min.$^{-1}$, but formate ion is a noticeable exception.

The figures in Table VII show that the acid catalytic constant k_A increases with K_A, as is to be expected, but the range of the accurate values for k_A is so small that it is not worth while attempting to find an empirical relation.

8. The Effect of Other Types of Basic Catalysts

All the basic catalysts so far mentioned have been molecules with one negative charge like hydroxyl ion. Further experiments were performed to show that basic molecules with other electric charges were also effective catalysts. The first uncharged basic molecule tried was aniline, but in this case there was some other reaction as well as the mutarotation; this showed itself by an initial contraction of the solution, the volume reaching a minimum value after about 35 minutes; it was nearly 80 minutes before the volume increase followed the unimolecular law. The disturbing process slowed down more rapidly than a unimolecular process and it therefore seemed probable that there was some combination between the aniline and the glucose, such a reaction being known to take place at high temperatures. Consequently one does not know the concentration of free aniline remaining and so no quantitative conclusions could be drawn from these experiments.

It was thought that with a tertiary base this disturbing reaction should be absent; experiments with pyridine pyridinium perchlorate buffer solutions gave quite normal results showing the pyridine molecule to have a catalytic constant $k_B = 82.2 \times 10^{-3}$ and the pyridinium ion to have no measurable effect. The results are given in Table VIII.

TABLE VIII

EXPERIMENTS WITH PYRIDINE (t = 18°)

Concn. of C_5H_5N	Concn. of $C_5H_5N.HClO_4$	$k \times 10^3$ min.$^{-1}$ obs.	$k \times 10^3$, calcd.
0.025	0.025	7.46	7.37
.050	.050	9.29	9.44
.050	.100	9.63	9.44
.050	.200	9.39	9.44
.050	.200	9.47	9.44

Ammonia being a much stronger base than pyridine, it would be expected to be a more powerful catalyst; it is in fact too strong a base for its effect to be accurately measured, because in ammonia-ammonium buffer solutions the hydroxyl effect will always be great unless the concentration of ammonium salt is great; the difficulty is analogous to that of measuring the effect of the undissociated cyanacetic acid molecules. It will be remembered that when we computed Osaka's data[19] for ammonia-ammonium chloride buffers (see Table I) and assumed hydroxyl ion to be the only catalyst other than water, we found that the solutions with high concentrations of NH_4^+ and NH_3 gave high results for the velocity constants. Now Osaka also performed three experiments in solutions containing ammonium chloride but no ammonia and these show that any possible effect of NH_4^+ up to a concentration of $6\text{–}7 \times 10^{-2}$ is undetectable. There remains the possibility of the NH_3 molecules being catalytically active and our experiments with pyridine make this probable. If we assume, as Hudson did in computing Osaka's results, that k_{NH_3} is zero, then the best value for k_{OH^-} is 9120, but if we do not make this unwarranted assumption we find that the data are best fitted by the formula

$$k = 0.0096 + 6200\, c_{OH^-} + 3.2 c_{NH_3}$$

This is shown in Table IX where k_1 is the value of k obtained from this formula and k_2 from the formula

$$k = 0.0096 + 9120\, c_{OH^-}$$

We do not in any way claim that the values we have assumed for k_{OH^-} and k_{NH_3} are accurate, but only that the k_1 values agree with the data appreciably better than the k_2 values. We shall later give independent evidence that the value chosen for k_{NH_3} is of the order of magnitude to be expected. The ammonia molecule is thus a catalyst about ten times as powerful as hydrogen ion.

Table IX

Osaka's Experiments Recomputed ($t = 25°$)

$c_{NH_4Cl} \times 10^2$	$c_{NH_3} \times 10^3$	$c_{OH^-} \times 10^6$	$k \times 10^2$ obs.	$k_1 \times 10^2$	$k_2 \times 10^2$
6.67	4.42	1.87	3.60	3.54	2.67
5.00	3.32	1.81	3.35	3.14	2.61
2.25	2.14	2.30	3.26	3.08	3.06
2.25	3.22	3.46	3.82	4.14	4.12
3.33	4.42	3.37	4.46	4.46	4.03
2.25	4.27	4.59	4.94	5.18	5.14
2.25	5.35	5.75	6.40	6.23	6.20
2.25	6.41	6.90	7.05	7.29	7.25

While only little is known about the strength of simple basic molecules with unit positive charge, there are a number of acid molecules with three positive charges whose dissociation constants have been determined quite accurately and their conjugate bases with two positive charges are very suitable for our purpose. The catalytic effect of two such ions was measured. The first was $[Co(NH_3)_5OH]^{++}$ of which the conjugate acid is the well-known roseo ion $[Co(NH_3)_5OH_2]^{+++}$. The second was the green ion $[Cr(OH_2)OH]^{++}$ conjugate to the blue acid $[Cr(OH_2)_6]^{+++}$ The results of these experiments are given in Table X. The last column

TABLE X

EXPERIMENTS TO DETERMINE THE EFFECT OF BASIC CATIONS (t = 18°)

Concn. of salt with basic cation		Concn. of salt with acid cation		Concn. of salt with neutral cation		$k\times10^3$ obs.	$k\times10^3$ calcd.
$[Co(NH_3)_5OH](ClO_4)_2$	0.0002	$[Co(NH_3)_5OH_2](ClO_4)_3$	0.020	$NaClO_4$	0.0002	5.49	5.46
$[Co(NH_3)_5OH](ClO_4)_2$	.0020	$[Co(NH_3)_5OH_2](ClO_4)_3$	.020	$NaClO_4$	.0020	6.82	6.86
$[Co(NH_3)_5OH](ClO_4)_2$	.0020	$[Co(NH_3)_5OH_2](ClO_4)_3$	.040	$NaClO_4$	.0020	6.82	6.86
$[Co(NH_3)_5OH](ClO_4)_2$	.0010	$[Co(NH_3)_5OH_2](ClO_4)_3$	.020	$NaClO_4$	.0010	6.13	6.08
$[Cr(OH_2)_5OH]Cl_2$	.0011	$[Cr(OH_2)_6]Cl_3$	.0009	NaCl	.0010	5.83	5.76
$[Cr(OH_2)_5OH]Cl_2$	.0021	$[Cr(OH_2)_6]Cl_3$	.0019	NaCl	.0020	6.38	6.18
$[Cr(OH_2)_5OH]Cl_2$	.0031	$[Cr(OH_2)_6]Cl_3$	.0029	NaCl	.0030	6.66	6.63
$[Cr(OH_2)_5OH]Cl_2$	.0041	$[Cr(OH_2)_6]Cl_3$	.0019	NaCl	.0040	6.87	6.98
$[Cr(OH_2)_5OH]Cl_2$	.0041	$[Cr(OH_2)_6]Cl_3$	.0039	NaCl	.0040	6.85	6.98
$[Cr(OH_2)_5OH]Cl_2$	.0051	$[Cr(OH_2)_6]Cl_3$	.0049	NaCl	.0050	7.31	7.38
				$[Co(NH_3)_6](NO_3)_3$	0.040	5.36	5.30

gives values calculated for k assuming that the acid ions are catalytically inactive while the basic ion $[Co(NH_3)_5OH]^{++}$ has a catalytic constant $k_B = 0.78$ (five times that of oxonium) and the basic ion $[Cr(OH_2)_5OH]^{++}$ has a catalytic constant[29] $k_B = 0.41$.

The last experiment in the table shows that the luteo ion $[Co(NH_3)_6]^{+++}$, whose structure is extremely similar to that of the roseo ion $[Co(NH_3)_5OH_2]^{+++}$ but which unlike the roseo ion is neutral, has no detectable effect. It appears that primary salt effect is negligible even with tervalent ions at the concentrations of these experiments.

The catalytic effect of bases with two positive charges is considerably greater than that of a base of the same strength with a negative charge. This agrees with the results obtained in the nitramide reaction, which is extremely sensitive to the influence of such ions.

Finally, as an example of a base with two negative charges, the sulfate ion was chosen. Whereas the acid constant of sulfuric acid is immeasurably great, that of the bisulfate ion[30] is 1.15×10^{-2}. Hence the sulfate ion SO_4^{--} is a somewhat weaker base than cyanacetate and would thus be expected to have only a small effect. Provided, however, this effect is not too small to be detected at all, it will be simpler to measure than that of, say, oxalate ion; for in order to suppress the hydroxyl-ion concentration in oxalate solutions one would have to have present, as well as $C_2O_4^{--}$, a quite considerable amount of HCO_4^-; but HCO_4^- is both an acid and a base and so its catalytic properties might not be simple. With sulfate solutions, however, the merest trace of excess acid is sufficient to keep the P_H well below 6. The solutions used were made up as follows. To a volume of standard sulfuric acid enough standard sodium hydroxide

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[29] A possible effect of the $[Cr(OH_2)_4(OH)_2]^+$-ion has been disregarded in this calculation.

[30] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926).

was added to make the solution just alkaline to methyl red; two or three drops of normal acetic acid were then added to bring the solution to the acid side of the methyl red end-point; the solution was then diluted to the required extent. The value found for $k_{SO_4^{--}}$ was 4.0×10^{-3}. The results are given in Table XI

TABLE XI

EFFECT OF SULFATE ION ($t = 18°$)

Concn. Na_2SO_4, moles per liter	Concn. of acetic acid	$k \times 10^3$ min.$^{-1}$ obs.	$k \times 10^3$ calcd.
0.050	10^{-4}	5.55	5.50
.075	10^{-4}	5.60	5.60
.100	10^{-4}	5.67	5.70

9. Interpretation of the Spontaneous Reaction and the Mechanism of Mutarotation

We have now obtained evidence that in dilute aqueous solution any molecule, charged or neutral, if a sufficiently strong base or acid, will increase the velocity of mutarotation in proportion to the concentration at which it is present. There remains the question of interpreting k_0 the minimum value of k, or constant of the "spontaneous" reaction in aqueous solution. It was suggested in the work of Brönsted and Pedersen[4a] that the "spontaneous" nitramide decomposition is actually a basic catalysis by the solvent molecules, and a similar interpretation in the case of the mutarotation seems very plausible. Much light is thrown on this question by the work of Lowry and others[31] on tetramethylglucose. This sugar has approximately the same rate of mutarotation in water as glucose and has the advantage of greater solubility in anhydrous solvents and can be obtained in a much purer state. Lowry and Richards have succeeded in showing that in dry ethyl acetate the mutarotation of tetramethylglucose could be arrested over a period of about 24 hours; in chloroform containing a trace of phosgene, which removes organic bases, an arrest was obtained over a period of 10 days. We do not wish to enter into a discussion of whether mutarotation takes place not at all or only extremely slowly in a pure inert solvent, but it is at any rate established that the actually observed minimum rate in water is due practically entirely to the water itself. In other words, the OH_2 molecule is a catalyst to which we can assign a catalytic constant $k_0/55.6 = 9.5 \times 10^{-5}$. (As in assigning values to the acid and basic constants of OH_2 we had to ignore the association of the water, we have to do the same in assigning a value to its catalytic constant; as our purpose is eventually to discuss the interdependence of these constants these errors will to some extent balance each other.) The next question that suggests itself is whether the OH_2 molecule acts

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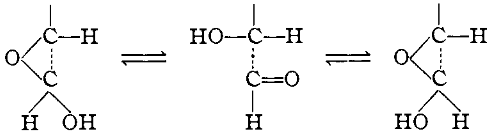
[31] (a) Lowry and Richards, *J. Chem. Soc.*, **127**, 1385 (1925). (b) Lowry and Faulkner, *ibid.*, **127**, 2883 (1925); (c) **128**, 1938 (1926).

as an acid or as a basic catalyst. This question has also been answered by Lowry[31b] who showed that the rate of mutarotation of tetramethylglucose in dry pyridine, a base, and in dry cresol, an acid, was less than 3% of its rate in water, but that by using as solvent mixtures of pyridine and cresol high rates could be obtained up to twenty times that in water. Lowry[28] interprets this to mean that both an acid molecule and a basic molecule take part in the reaction. It is generally agreed among organic chemists that in the change from α-glucose to β-glucose the aldehyde form of glucose is an intermediate product.



There is a considerable difference of opinion as to which of these three forms may be hydrated, but this question need not concern us. The fact that mutarotation follows the unimolecular law can be simply interpreted only by assuming that the change from the α- or β-form to the aldehyde form is slow compared with the change from the aldehyde form to either of the others. Thus the observable rate of the mutarotation is determined by the velocities of the change from α- or β-form to aldehyde form, processes involving only a change of position of one proton. Lowry's[28] interpretation of the mechanism of the catalysis is that the basic catalyst removes a proton from one part of the glucose molecule and the acid catalyst supplies a proton to another part of the molecule. If we write symbolically HG for α-glucose and GH for the aldehyde form, then the mechanism of the primary process in water is, in the absence of other catalysts

$$OH_2 + H\ \ G + H \vdots OH \longrightarrow OH_3^+ + GH + OH^-$$

where one OH_2 molecule acts as an acid and one as a base. In catalysis by oxonium ion OH_3^+, or by an undissociated molecule of mandelic acid MH, an OH_2 molecule acts as a base.

$$OH_2 + H \vdots G + H \vdots OH_2^+ \longrightarrow OH_3^+ + GH + H_2O$$
$$OH_2 + H \vdots G + H \vdots M \longrightarrow OH_3^+ + GH + M^-$$

In catalysis by hydroxyl ion OH^-, or by acetate ion Ac^- or by the pyridine molecule Py, one molecule of OH_2 acts as an acid.

$$OH^- + H\ \ G + H \vdots OH \longrightarrow OH_2 + GH + OH^-$$
$$Ac^- + H \vdots G + H \vdots OH \longrightarrow AcH + GH + OH^-$$
$$Py + H \vdots G + H \vdots OH \longrightarrow PyH^+ + GH + OH^-$$

We have given these processes in some detail because, while entirely agreeing with Lowry as to the reasonableness of this mechanism, we consider that in his own description of it there is some confusion between the catalytic effect of the hydroxyl ion in an aqueous solution of pyridine and the effect of the pyridine molecule itself; except in solutions containing very little water the former effect will be the greater of the two. We also wish to emphasize the similar catalytic action of the various bases, regardless of their electric charge, and likewise the similar catalytic action of the several types of acids.

10. The Interrelation between Strength and Catalytic Effect of Acids and Bases

The question of an interrelation between the strength and the catalytic activity of acids and bases has already been considered in Section 7 for the case of univalent basic anions. Evidence from the later sections permits of a more general discussion of this problem and also a very considerable extension of the region of acidity and basicity considered.

The data for typical acid and basic catalysts of various types are given in Table XII. The first two columns give a number of conjugate acid-base pairs of various types; the third column gives values of K_A for the acid; the fourth gives the catalytic constant k_A for the acid and the fifth the catalytic constant k_B for the base. In Fig. 6, log k_A and log k_B are plotted against log K_A. Included in the table are the values of k_B for hydroxyl ion and the ammonia molecule computed from Osaka's data; these values are halved in the plot because Osaka's experiments were at 25° whereas our own were at 18°, a correction which is not of great importance.

TABLE XII

CATALYTIC CONSTANTS (t = 18°)

Acid	Base	K_A	k_A	k_B
OH_3^+	OH_2	5.6×10	1.4×10^{-1}	9.5×10^{-5}
OH_2	OH^-	1.0×10^{-16}	9.5×10^{-5}	[a]6×10^3
Mandelic acid	Mandelate ion	4.3×10^{-4}	6×10^{-3}	1.1×10^{-2}
Acetic acid	Acetate ion	1.8×10^{-5}	2×10^{-3}	2.7×10^{-2}
Pyridinium ion	Pyridine	3.5×10^{-6}		8.3×10^{-2}
$[Co(NH_3)_5OH_2]^{+++}$	$[Co(NH_3)_5OH]^{++}$	1.6×10^{-6}		7.8×10^{-1}
Ammonium ion	Ammonia	3.2×10^{-10}		[a]3.2
HSO_4^-	SO_4^{--}	1.2×10^{-2}		4×10^{-3}

[a] At 25°.

The plot shows the points corresponding to basic catalysis to lie approximately on a straight line except for the bases having a double positive charge. The slope of this line is 0.42, while for univalent anions, as mentioned, the slope 0.34 was found. The values for OH^- and OH_2, however, are uncertain for several reasons. For instance, in basic solution, in addition to the OH^- ion, there will exist strongly basic glucose anions which may have a considerable catalytic effect and so make the OH^- ion appear more effective than it actually is. It should be noted also that no attention has been paid here to the influence of statistical factors,[2,4a] such as would be necessary for the establishment of an exact relation between the strength and the catalytic effect of an acid or base.

The position of the point for the NH_3 molecule justifies our belief that the value computed from Osaka's data is at least of the right order of magnitude.

The basic molecules with two positive charges seem to possess a particularly strong basic effect. This agrees with the results found in the nitramide catalysis and also with theoretical considerations.[2]

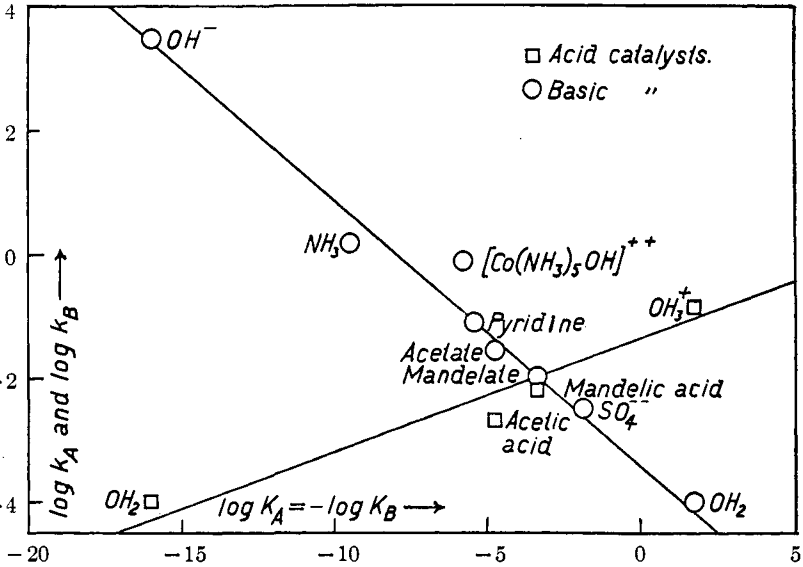


Fig. 6.—Dependence of acid and basic catalysis on the strength of acid and base.

The curve for acid catalysis is not so well established as the one for basic catalysis, but the increasing catalytic effect with increasing acid strength is obvious. When one considers that the plot covers a range of 10^{18} in K_A and of 10^8 in k_B, the connection between the catalytic effect of an acid or base and its strength is striking. It indeed appears that one could predict the catalytic effect, at least correct to one power of 10, of any acid or basic molecule or ion merely from the knowledge of its strength.

Summary

1. In correspondence with an extended conception of acids and bases a new theory of acid and basic catalysis has been presented, in which the catalytic effect is ascribed, not particularly to the hydrogen and hydroxyl ion, but to the action of acid and basic molecules in general. Previous work in the field has been discussed and criticized.

2. The mutarotation reaction of glucose has been studied by a dilato-

metric method under the influence of a number of acids and bases of various electric charge types. The results of the experiments have given strong support to the theory presented.

3. The catalytic effect of acid and basic molecules on the mutarotation of glucose increases with their strength as acids and bases. There seems to be a simple relationship between catalytic efficiency and strength, shown by the fact that a logarithmic plot of the basic catalytic constant against the basic strength constant, covering the range of 10^{18} in the latter, comes out approximately as a straight line with slope about 0.4.

4. The laws of mutarotation are in marked conformity with the laws previously found for the decomposition of nitramide.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCTION OF BENZIL BY THE BINARY SYSTEM, MAGNESIUM + MAGNESIUM IODIDE (OR BROMIDE)

BY M. GOMBERG AND W. E. BACHMANN

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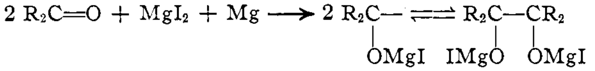
Recently we described the reducing action of a mixture of magnesium iodide (or bromide) and magnesium on aromatic ketones.[1] This class of ketones was found to give pinacolates through the intermediate formation of free radicals, ketyls



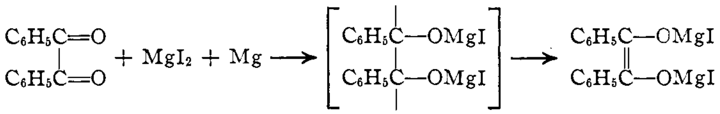
$$2\,\mathrm{R_2C{=}O} + \mathrm{MgI_2} + \mathrm{Mg} \longrightarrow 2\,\underset{\mathrm{OMgI}}{\mathrm{R_2C}}\!— \rightleftharpoons \underset{\mathrm{IMgO}}{\mathrm{R_2C}}—\underset{\mathrm{OMgI}}{\mathrm{CR_2}} \qquad (1)$$

According to our hypothesis, the active reducing agent was magnesium subiodide, generated by the interaction of the metal and halide

$$\mathrm{Mg} + \mathrm{MgI_2} \rightleftharpoons 2\,\mathrm{MgI} \qquad (2)$$

and present as such only in minute quantities at any one moment. The reaction has now been extended to the diketone, benzil.

Benzil with its two carbonyl groups reacts with the binary system fundamentally in much the same fashion as do the aromatic ketones, except that here the newly created carbon-carbon bond remains within the original molecule, giving rise, therefore, to an unsaturated glycolate.



$$\begin{array}{l}\mathrm{C_6H_5C{=}O}\\ \quad|\\ \mathrm{C_6H_5C{=}O}\end{array} + \mathrm{MgI_2} + \mathrm{Mg} \longrightarrow \left[\begin{array}{l}\mathrm{C_6H_5\overset{|}{C}—OMgI}\\ \quad\ \ |\\ \mathrm{C_6H_5\underset{|}{C}—OMgI}\end{array}\right] \longrightarrow \begin{array}{l}\mathrm{C_6H_5C—OMgI}\\ \quad\ \ \|\\ \mathrm{C_6H_5C—OMgI}\end{array} \qquad (3)$$

The reaction proceeds *quantitatively* according to the above equation. In the process of reduction the solution displays a series of deep colors, green, brown, red and finally yellow. The halomagnesium glycolate

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[1] (a) Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927); (b) Gomberg, *Chem. Reviews*, **2**, 309 (1925).