84. *Reaction-kinetic Investigations of the Incomplete Dissociation of Salts. Part I. The Decomposition of Diacetone Alcohol in Solutions of Metallic Hydroxides.*

By R. P. BELL and J. E. PRUE.

It is shown that measurements of reaction velocities may provide a useful method for estimating the degree of dissociation of salts in solution. Data are given for the rate of decomposition of diacetone alcohol in solutions of sodium, potassium, rubidium, calcium, barium, and thallous hydroxides. Values derived for the dissociation constants of the species $CaOH^+$, $BaOH^+$, and TlOH are in fair agreement with values obtained from other sources. It is concluded that the formation of $CaOH^+$ and $BaOH^+$ can be reasonably accounted for on electrostatic grounds, but that TlOH must involve covalent binding.

THE interionic attraction theory gives a satisfactory account of the thermodynamic behaviour of very dilute salt solutions, but the physical and mathematical approximations employed break down as the concentration increases, especially for small ions. Attempts have been made to carry the mathematical approximations of the Debye–Hückel theory a stage further (Gronwall, *Proc. Nat. Acad. Sci.*, 1927, **13**, 198; Gronwall, LaMer, and Sandved, *Physikal. Z.*, 1928, **29**, 358), but these lead to inconsistencies which show that the physical bases of the treatment are too crude to warrant such refinement (cf., *e.g.*, Guggenheim and Fowler, "Statistical Thermodynamics", p. 407, Cambridge, 1939). An analysis of the experimental data shows

(Brönsted, *J. Amer. Chem. Soc.*, 1922, **44**, 877; Guggenheim, *Phil. Mag.*, 1935, **19**, 588) that the individual deviations of electrolytes from the simple Debye–Hückel theory depend essentially on the short-range interactions between pairs of ions of opposite charge. Part of these deviations can be described by supposing that a certain fraction of the electrolyte is undissociated, and behaves like a non-electrolyte (or, in the case of an unsymmetrical electrolyte, like an ion of reduced charge), while the free ions obey the simple Debye–Hückel law. This idea was first introduced by Bjerrum (*Kgl. Danske Vid. Selsk. Mat.-fys. Medd.*, 1926, **7**, No. 9) and shown to account successfully for the activity coefficients and conductivities of many electrolytes, and his treatment was further developed by Fuoss (*Trans. Faraday Soc.*, 1934, **30**, 967). These authors treated ionic association as a purely electrostatic phenomenon, but it has been shown by Davies (*e.g.*, *J.*, 1938, 276; 1939, 349, and earlier papers) that consistent values for the dissociation constants of many " strong " electrolytes can be derived from experimental data without making assumptions about the nature of the forces involved.

In deriving these values it is necessary to ascribe to incomplete dissociation all deviations from ideal or standard behaviour, and considerable difficulty arises in the choice of such standards for different properties of electrolyte solutions. There has therefore been some difference of opinion as to the status of the dissociation constants obtained: for example, they have been described as having " more of the nature of an adjustable mathematical parameter than a definite physical entity " (Owen and Gurry, *J. Amer. Chem Soc.*, 1938, **60**, 3074). This view might be justified if the concept of incomplete dissociation were successful only in accounting for thermodynamic properties. However, it has been shown by Davies (*loc. cit.*) that the same dissociation constants will also account for the conductivity data, and in some cases yet other properties of salt solutions (*e.g.*, optical rotation). It is the purpose of the present series of papers to investigate how far the velocities of reactions involving salts can be similarly interpreted in terms of incomplete dissociation.

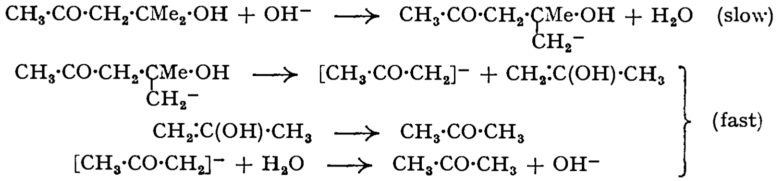
When an ion of a strong electrolyte takes part in a reaction with a neutral molecule (either as a reactant or as a catalyst) the reaction velocity is usually more closely proportional to the concentration of the ion than to its activity (cf. Bell, " Acid–Base Catalysis ", p. 13, Oxford, 1941). This suggests that, when the ion is present as a salt which is incompletely dissociated, the reaction velocity may be used as a measure of its true concentration. The problem can be expressed more precisely in terms of the transition-state theory of reaction velocity. If an ion X^-, present as a salt XY, is reacting with an uncharged molecule S, the reaction velocity expression will contain the stoicheiometric concentrations of X^- and S, multiplied by an activity coefficient factor $f_S f_{X^-}/f_{XS^-}$, where XS^- is the transition state. In fairly dilute solutions f_S will be effectively unity, and, since X^- and XS^- have the same charge, f_{X^-}/f_{XS^-} will also be close to unity in the absence of any specific interaction between Y^+ and X^- or XS^-: hence in this case the reaction velocity will be directly proportional to the stoicheiometric concentration of X^-, as is found in many cases. If, on the other hand, either X^- or XS^- or both interact specifically with Y^+, the term f_{X^-}/f_{XS^-} must be retained. In particular, if X^- interacts specifically with Y^+ but XS^- does not (*e.g.*, if XSY is completely dissociated and XY is not), then the reaction-velocity expression will contain a factor representing only the specific part of the interaction between X^- and Y^+. The kinetic method should thus lead to the same degrees of dissociation as other methods provided that we can neglect the association of the transition state XS^- with any oppositely charged ions. This is likely to be the case, since the transition state will always be larger than the ion X^-, and its charge is often spread over several atoms, but it cannot be assumed without experiment. For catalytic reactions the statement that Y^+ does not interact specifically with the transition state is equivalent to saying that there is no catalysis by the species XY, so that the most suitable reactions for the present purpose are likely to be those which exhibit specific catalysis by hydrogen or hydroxyl ions rather than general acid–base catalysis.

The reaction studied in the present paper is the depolymerisation of diacetone alcohol, which has long been known as an instance of specific hydroxyl-ion catalysis (Koelichen, *Z. physikal. Chem.*, 1900, **33**, 129; Akerlöf, *J. Amer. Chem. Soc.*, 1926, **48**, 3046; 1927, **49**, 2955; 1928, **50**, 1279; LaMer and Miller, *ibid.*, 1935, **57**, 2674). Previous investigators have shown that in solutions of sodium and potassium hydroxides the reaction velocity is directly proportional to the stoicheiometric hydroxyl-ion concentration up to about 0·1N, but that barium hydroxide gives velocities as much as 7% lower (Koelichen, *loc. cit.*). Since Davies has derived a value of about 0·2 for the dissociation constant $[Ba^{++}][OH^-]/[BaOH^+]$, this difference is of the expected order of magnitude. A similar effect would be expected for calcium hydroxide, and we have also investigated thallium hydroxide, for which Ostwald (*J. pr. Chem.*, 1887, **35**, 114) found a conductivity–concentration curve differing considerably from those of the alkali-metal hydroxides, suggesting incomplete dissociation.

There is some difference of opinion as to the kinetic mechanism of the diacetone alcohol depolymerisation. The more probable scheme is that suggested by Hammett (" Physical Organic Chemistry ", p. 344, New York 1940), *i.e.* :

$$\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}OH + OH^- \rightleftharpoons CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}O^- + H_2O} \quad \text{(fast)}$$
$$\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}O^- \longrightarrow [CH_3{\cdot}CO{\cdot}CH_2]^- + COMe_2} \quad \text{(slow)}$$
$$\mathrm{[CH_3{\cdot}CO{\cdot}CH_2]^- + H_2O \longrightarrow COMe_2 + OH^-} \quad \text{(fast)}$$

On the other hand, Butler and Nelson (*J.*, 1938, 957) have suggested the following alternative mechanism on the basis of the hydrogen isotope effect :



$$\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CMe_2{\cdot}OH + OH^- \longrightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}\underset{CH_2^-}{C}Me{\cdot}OH + H_2O} \quad \text{(slow)}$$
$$\left.\begin{array}{l}\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}\underset{CH_2^-}{C}Me{\cdot}OH \longrightarrow [CH_3{\cdot}CO{\cdot}CH_2]^- + CH_2{:}C(OH){\cdot}CH_3} \\ \mathrm{CH_2{:}C(OH){\cdot}CH_3 \longrightarrow CH_3{\cdot}CO{\cdot}CH_3} \\ \mathrm{[CH_3{\cdot}CO{\cdot}CH_2]^- + H_2O \longrightarrow CH_3{\cdot}CO{\cdot}CH_3 + OH^-}\end{array}\right\} \text{(fast)}$$

For our present purpose the distinction between the two mechanisms is not an important one, since in each of them the transition state is a large organic species bearing one negative charge.

EXPERIMENTAL.

Diacetone alcohol was obtained by redistilling a commercial preparation under 30 mm. pressure, and was stored in hard-glass vessels. It contained not more than 4 × 10^{-4} mole of free acid per 100 g.

TABLE I.

(c = concentration in g.-equiv./l.)

Sodium hydroxide.

c(NaOH) ...	0·01046	0·02093	0·02616	0·03139	0·04186	0·05005	0·05181	0·0751	0·1001
$10^3k/[OH^-]$ *	218·0	216·7	217·9	218·0	216·7	217·0	217·3	216·1	214·6
c(NaOH) ...	0·1335	0·1668	0·2002	0·2336	0·2669	0·3003	0·3337	0·3671	0·4002
$10^3k/[OH^-]$ *	212·7	211·6	211·1	210·3	209·0	207·8	207·1	205·6	205·1

cNaOH + $\frac{1}{2}c$NaCl.

c(NaOH)	0·0508	0·1016	0·1524	0·2002	0·2708	0·3337	0·3809
$10^3k/[OH^-]$ *	214·0	211·8	207·7	205·6	203·8	200·8	200·3

Potassium hydroxide.

c(KOH) ...	0·1633	0·2449	0·3266	0·3592	0·3918
$10^3k/[OH^-]$ *	216·8	217·6	216·5	216·6	217·7

cKOH + $\frac{1}{2}c$KCl.

c(KOH) ...	0·0816	0·1633	0·2612	0·3102	0·3674
$10^3k/[OH^-]$ *	215·7	213·7	210·6	210·8	209·0

Rubidium hydroxide.

c(RbOH)	0·0674	0·1679	0·2686	0·3021	0·3324
$10^3k/[OH^-]$ * ...	217·8	218·5	219·3	218·9	218·7

cRbOH + $\frac{1}{2}c$RbCl.

c(RbOH)	0·1007	0·2014	0·3021
$10^3k/[OH^-]$ * ...	215·6	213·9	212·8

Calcium hydroxide.

$c[Ca(OH)_2]$	0·01442	0·01802	0·02162	0·02523	0·02882	0·03243	0·03569
$10^3k/[OH^-]$ *	203·8	201·9	202·1	197·3	197·3	193·4	194·2

0·025NaOH + cCaCl$_2$ + (0·175 − 3c/2)NaCl.

(Ionic strength = 0·2 throughout.)

$c(CaCl_2)$	0	0·0200	0·0400	0·0700	0·0900
$10^3k/[OH^-]$ *	200·0	191·3	184·1	173·2	168·5

Barium hydroxide.

$c[Ba(OH)_2]$	0·04605	0·07402	0·09870	0·1316	0·1645	0·1974
$10^3k/[OH^-]$ *	208·4	204·3	197·5	194·5	190·3	185·5
$c[Ba(OH)_2]$	0·2303	0·2632	0·2961	0·3290	0·3619	0·3948
$10^3k[OH^-]$ *	184·5	182·7	179·7	178·7	176·3	173·8

Thallous hydroxide.

c(TlOH)	0·02050	0·04099	0·08882	0·1298	0·1708	0·2186	0·2665	0·3075	0·3383
$10^3k/[OH^-]$ * ...	212·1	204·2	192·1	185·0	175·8	169·4	165·1	162·7	158·1

Since the kinetic experiments were carried out with approximately 1% solutions, this amount of acid would cause an error of less than 0·5% in the most dilute solutions of alkali employed. Solutions of sodium, potassium, calcium, and barium hydroxides were prepared from the pure solids. Solutions of the hydroxides of thallium and rubidium were prepared by treating solutions of thallous sulphate and rubidium chromate respectively with a very slight excess of barium hydroxide solution. All hydroxide solutions were standardised against constant-boiling hydrochloric acid, and conductivity water was used throughout, strict precautions being taken to exclude carbon dioxide.

The kinetic measurements were made at 25° ± 0·01° in a simple dilatometer of about 25 c.c. capacity with a capillary 0·5 mm. in diameter. In order to prevent the formation of air bubbles, the hydroxide solutions were evacuated for a few minutes before use. After ten minutes in the thermostat the diacetone alcohol was added from a small automatic pipette, and the dilatometer filled by suction. Reliable readings could be obtained 8 minutes after mixing. The reactions were throughout strictly of the first order, and the velocity constants were calculated by the method of Guggenheim (*Phil. Mag.*, 1926, **7**, 538), their accuracy being estimated as about ±0·5%.

Results.—Table I gives values of the apparent catalytic constants $k/[\mathrm{OH}^-]^*$ where k is the first-order velocity constant in terms of decadic logarithms and minutes, and $[\mathrm{OH}^-]^*$ is the stoicheiometric concentration of hydroxyl ions in moles per litre, complete dissociation of the metallic hydroxides being assumed. Some measurements were carried out with mixtures of the type cNaOH + $\frac{1}{2}c$NaCl in order to obtain data for comparison with $Ba(OH)_2$ solutions of the same $[\mathrm{OH}^-]^*$ and the same ionic strength.

DISCUSSION.

(a) *Alkali Hydroxides.*—Fig. 1 shows a plot of the observed catalytic constant $k/[\mathrm{OH}^-]^*$ against the stoicheiometric hydroxyl-ion concentration for the hydroxides of sodium, potassium, and rubidium. It will be seen that they all converge to the same value at infinite dilution, namely $0{\cdot}218_2$. This value is higher than those obtained by most previous workers (*e.g.*, French, *J. Amer. Chem. Soc.*, 1929, **51**, 3215; Murphy, *ibid.*, 1931, **53**, 977; Sturtevant, *ibid.*, 1937, **59**, 1534), but slightly lower than the value $0{\cdot}221_9$ given by LaMer and Miller (*loc. cit.*). These authors attribute values lower than their own to contamination by carbon dioxide or to impurities in the diacetone alcohol used, but this does not seem a likely explanation in our case in view of the good reproducibility with different samples of alkali and diacetone alcohol.

FIG. 1.

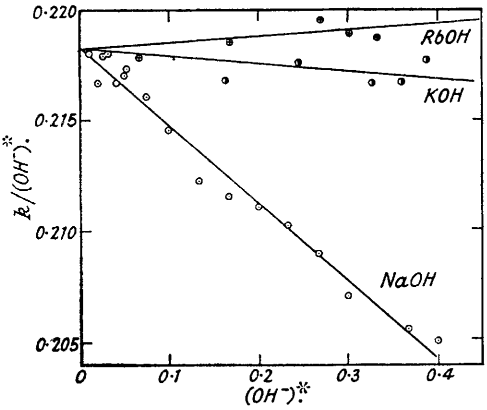
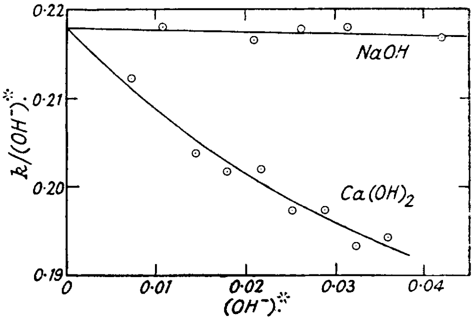


FIG. 2.



At higher concentrations potassium and rubidium hydroxides show respectively a slight decrease and a slight increase in catalytic constant, but this is barely greater than the experimental error of about 0·5%. On the other hand, sodium hydroxide shows a marked decrease in catalytic effect with increasing concentration, amounting to about 7% in 0·4N-solution. The same effect has been found by Akerlöf at higher concentrations, and analogous differences occur in the activity coefficients. Thus the tables compiled by Harned and Robinson (*Chem. Reviews*, 1941, **28**, 419) show that the mean activity coefficients of potassium and cæsium hydroxides are closely similar up to about 0·5N, while sodium hydroxide gives values up to 8% lower: similarly, indicator measurements by Schwarzenbach and Sulzberger (*Helv. Chim. Acta*, 1944, **27**, 348) indicate that concentrated solutions of potassium hydroxide are more strongly alkaline than corresponding solutions of sodium hydroxide. Both the kinetic and the thermodynamic data could be formally accounted for by supposing that sodium hydroxide differs from the other alkali hydroxides in being incompletely dissociated, but the dissociation constant involved would be so large (*ca.* 5) that it is doubtful whether this interpretation is a useful one. For present purposes we shall only conclude that at higher concentrations potassium and rubidium hydroxides provide a better standard of " normal behaviour " than does sodium hydroxide.

(b) *Calcium Hydroxide.*—The catalytic constants for this hydroxide are plotted against $[OH^-]^*$ in Fig. 2, together with those for sodium hydroxide for comparison. (In the relevant concentration range there is no appreciable variation of $k/[OH^-]^*$ for any of the alkali hydroxides, so that it is immaterial which of them is used for comparison.) Both curves extrapolate to the same point at infinite dilution, but at the highest concentration the catalytic effect of the calcium hydroxide solutions has decreased by about 12%. The data given by Davies (*loc. cit.*) for the dissociation constant of $CaOH^+$ and its variation with ionic strength indicate a deficiency of 12·6% in the concentration of hydroxyl ions in this solution. It therefore seems likely that the kinetic results can also be accounted for on the basis of incomplete dissociation.

If we assume that the true hydroxyl-ion concentration is given by $[OH^-] = k/0{\cdot}2182$, we can obtain $[CaOH^+] = [OH^-]^* - [OH^-]$, and hence the concentration dissociation constant $K_c = [Ca^{++}][OH^-]/[CaOH^+]$. These values are given in the first columns of Table II.

TABLE II.

Calcium hydroxide.

$[OH^-]$.*	$[OH^-]$.	$[CaOH^+]$.	$[Ca]^{++}$.	K_c.	I.	K_d'.
0·01442	0·01347	0·00095	0·00626	0·095	0·0197	0·050
0·01802	0·01668	0·00134	0·00767	0·101	0·0244	0·052
0·02162	0·02006	0·00156	0·00925	0·122	0·0293	0·059
0·02523	0·02282	0·00241	0·01020	0·102	0·0330	0·047
0·02882	0·02607	0·00275	0·01166	0·116	0·0377	0·052
0·03243	0·02874	0·00369	0·01253	0·102	0·0413	0·044
0·03569	0·03176	0·00393	0·01392	0·117	0·0457	0·050
					Mean K_d' =	0·051

The thermodynamic dissociation constant K_d differs from K_c by the inclusion of the activity coefficient factor $f_{Ca^{++}}f_{OH^-}/f_{CaOH^+}$. (The values for $f_{Ca^{++}}$ and f_{OH^-} are here of course the " true " rather than the stoicheiometric values: *i.e.*, they apply only to the unassociated ions Ca^{++} and OH^-.) In the absence of data for these activity coefficients we have used the standard expression suggested by Guggenheim (*Phil. Mag.*, 1935, **19**, 588) for the activity coefficient of a z-valent ion at an ionic strength I, *viz.*,

$$-\log_{10}f_z = 0{\cdot}5z^2I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We can then define an approximate thermodynamic constant K_d' by

$$\log_{10}K_d' = \log_{10}K_c - 2I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the values of this constant are given in the last column of Table II. They show no trend with concentration, and the deviations of individual values are not greater than would arise from an error of ±0·5% in the kinetic measurements. It is therefore likely that the mean value of 0·051 is close to the true thermodynamic constant K_d, and this view is supported by the data given in Table I for mixtures of NaOH, NaCl, and $CaCl_2$. In these experiments the ionic strength was 0·2 throughout, and we have therefore taken as the standard catalytic constant the value for 0·025N-NaOH + 0·175N-NaCl, *i.e.*, $0{\cdot}200_0$. The true concentrations of hydroxyl ions are then calculated from $[OH^-] = k/0{\cdot}200$, and the remainder of the calculation is as before. The resulting values of K_d' are 0·047, 0·051, 0·049, 0·053; mean = 0·050. The excellent agreement with the former result is probably fortuitous in view of the uncertainty as to the correct value to take for the standard catalytic constant in these solutions.

The only other experimental data on the dissociation constant of $CaOH^+$ are those of Kilde (*Z. anorg. Chem.*, 1934, **218**, 118) on the effect of alkali on the solubility of calcium iodate. These data refer to ionic strengths of $I = 0{\cdot}05$—$0{\cdot}15$, and Kilde used an expression of the form (3)

$$-\log_{10}f_z = 0{\cdot}5z^2I^{\frac{1}{2}} + BI \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for extrapolating to zero ionic strength, obtaining $K_d = 0{\cdot}040$. Davies (*loc. cit.*) recalculated Kilde's results, introducing a correction for the incomplete dissociation of $CaIO_3^+$ and KIO_3, and used (4) for the activity coefficients. In this way he obtained $K_d = 0{\cdot}030$. The dissociation

$$-\log_{10}f_z = 0{\cdot}5z^2\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) + BI\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

constants of both these authors involve a large extrapolation, and hence depend considerably on the values adopted for the parameter B. It is therefore uncertain whether the differences between their values and our own value of 0·051 are significant. It should, however, be pointed out that the kinetic method will yield too high values for the degree of dissociation if there is some association between the transition state and the calcium ion, and this might account for the somewhat higher value which we have obtained.

(c) *Barium Hydroxide.*—The catalytic constants for this hydroxide are shown in Fig. 3. In treating these data two difficulties arise which were not present for calcium hydroxide. In the first place, since the stoicheiometric hydroxyl-ion concentrations extend up to 0·4N, there is some latitude in the choice of standard catalytic constants for calculating the true concentrations of hydroxyl ions. We have made calculations on two different assumptions : (i) That the true catalytic constant is throughout $0{\cdot}218_2$, *i.e.*, the value applicable to all hydroxides in very dilute solution. (ii) That the true catalytic constant of the hydroxyl ion in a barium hydroxide solution is the same as the observed constant in a mixture of KOH + KCl having the same stoicheiometric hydroxyl-ion concentration and the same ionic strength.

The hydroxyl-ion concentrations calculated from these two assumptions are given in cols. 2 and 3 of Table III, and cols. 4 and 5 give the corresponding values of $K_c = [\mathrm{Ba}^{++}][\mathrm{OH}^-]/[\mathrm{BaOH}^+]$. The data for the most dilute solution in Table I have been omitted from Table III, since the degree of association is very small and liable to considerable error. Both assumptions lead to a reasonably consistent set of values for K_c, with some tendency to increase with increasing ionic strength. However, the value of K_d must be considerably lower than those of K_c, since the lowest ionic strength concerned is about 0·1, and it is difficult to make correct allowance for the ionic activity coefficients in such concentrated solutions. Equation (1) will not be valid, but an expression like (4) is likely to apply at least to the more dilute solutions. We have therefore plotted $\log_{10}K_d$, [as defined by (2)] against I, and made a linear extrapolation to $I = 0$. The resulting plot is shown in Fig. 4, the vertical lines representing the error which would result from an error of ±0·5% in the kinetic measurements. The linear extrapolations give $K_d = 0{\cdot}21$ and $K_d = 0{\cdot}24$ for assumptions (i) and (ii) respectively.

FIG. 3.

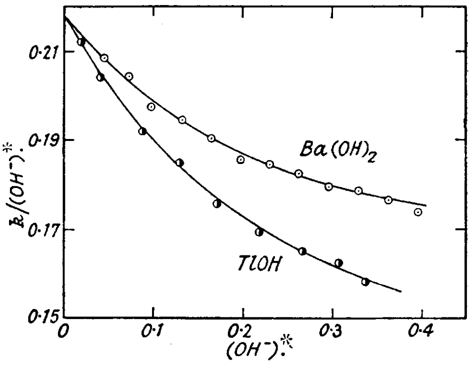


TABLE III.

Barium hydroxide.

	$[\mathrm{OH}^-]$.		K_c.		$-\log_{10} K_d'$.		I.	
$[\mathrm{OH}^-]$.*	(i.)	(ii).	(i).	(ii).	(i).	(ii).	(i).	(ii).
0·0740	0·0688	0·0696	0·42	0·40	0·855	0·776	0·101	0·102
0·0987	0·0894	0·0906	0·38	0·46	0·947	0·871	0·129	0·132
0·1316	0·1173	0·1193	0·42	0·52	0·957	0·872	0·169	0·173
0·1645	0·1434	0·1442	0·42	0·49	1·004	0·920	0·205	0·210
0·1974	0·1677	0·1715	0·39	0·48	1·055	0·979	0·227	0·244
0·2303	0·1947	0·1997	0·44	0·55	1·049	0·951	0·274	0·285
0·2632	0·2204	0·2268	0·43	0·59	1·055	0·951	0·309	0·322
0·2961	0·2438	0·2516	0·47	0·59	1·087	0·979	0·340	0·355
0·3290	0·2695	0·2787	0·45	0·60	1·082	0·970	0·375	0·393
0·3619	0·2923	0·3050	0·47	0·63	1·107	0·994	0·404	0·425
0·3948	0·3130	0·3251	0·44	0·59	1·145	1·029	0·429	0·453

These values may be compared with $K_d = 0{\cdot}23$ derived by Davies (*loc. cit.*) from the activity coefficient data of Harned and Masson (*J. Amer. Chem. Soc.*, 1932, **54**, 1441). The differences between the three values are not greater than the experimental and theoretical uncertainties of both methods. Davies's method for deriving degrees of association involves the assumption that all other interionic forces can be satisfactorily represented by equation (4), giving B the universal value $-0{\cdot}20$. The slopes of our extrapolations in Fig. 4 correspond to a much greater value of B (*ca.* $-0{\cdot}8$), and values of K_c calculated by Davies's method indicate a value of B considerably greater than $-0{\cdot}2$ if the data at higher concentrations are included. If a higher value of B were used throughout in Davies's calculations this would bring his values of K_c at higher concentrations into closer agreement with our own, but would not appreciably affect the extrapolated value of K_d.

(d) *Thallous Hydroxide.*—The plot of catalytic constant against $[OH^-]^*$ is given in Fig. 3. This hydroxide is of the same charge type as potassium and rubidium hydroxides, and since the latter deviate inappreciably from the limiting value $k/[OH^-]^* = 0{\cdot}218_2$ in the relevant concentration range, we have used this value in calculating the true values of $[OH^-]$ in Table IV. The values of K_c obtained are again reasonably consistent. In extrapolating to obtain K_d we have used K_d' as defined by equation (2) with the omission of the factor 2. Fig. 5 shows a plot of $-\log_{10}K_d'$ against I, with vertical lines corresponding again to $\pm 0{\cdot}5\%$ in the kinetic measurements. The extrapolated value corresponds to $K_d = 0{\cdot}38$.

The only other data for comparison with this value are Ostwald's conductivity measurements (*loc. cit.*). Since the mobilities of the ions Tl^+ and K^+ are almost identical, it is a reasonable assumption to take $\Lambda(TlOH)/\Lambda(KOH)$ at equal ionic concentrations as equal to the degree of dissociation of TlOH. Values of $-\log_{10}K_d'$ calculated on this assumption are plotted in Fig. 5, and agree fairly well with those derived from the kinetic data, though if taken alone they suggest a somewhat lower value of K_d, *ca.* 0·32.

FIG. 4.

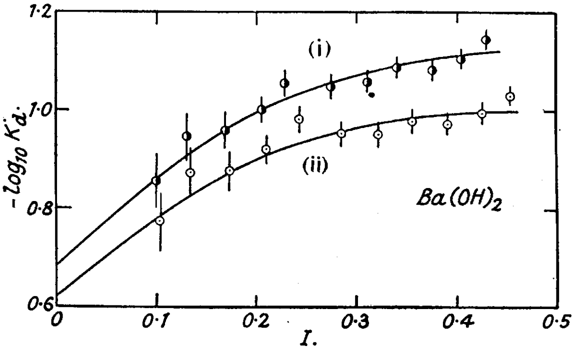


FIG. 5.

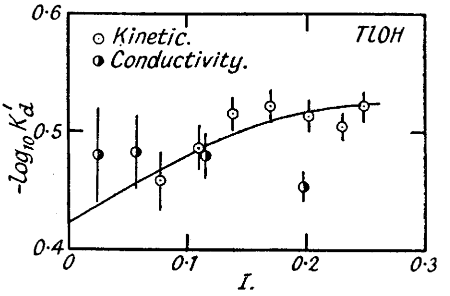


TABLE IV.

Thallous hydroxide.

$[OH^-]$.*	$[OH^-] = [Tl^+] = I$.	K_c.	$-\log_{10}K_d'$.	$[OH^-]$.*	$[OH^-] = [Tl^+] = I$.	K_c.	$-\log_{10}K_d'$.
0·0888	0·0782	0·59	0·459	0·2186	0·1697	0·60	0·522
0·1298	0·1092	0·58	0·486	0·2665	0·2017	0·63	0·512
0·1708	0·1376	0·57	0·515	0·3075	0·2292	0·67	0·503
0·2186	0·1697	0·60	0·522	0·3383	0·2452	0·63	0·521

General Conclusions.—The above data show that the kinetic method gives values for the degree of association of several metallic hydroxides which are in reasonable agreement with values derived by other methods. This justifies the assumption underlying the kinetic method, that the transition state in our reaction does not associate appreciably with the metallic ions present. It is of course by no means established that the same conclusion will hold good for other reactions or other solvents. For example, Schattenstein (*Acta Physicochim. U.R.S.S.*, 1935, **3**, 37; *J. Amer. Chem. Soc.*, 1937, **59**, 432) has studied the ammonolysis of santonin in liquid ammonia by a number of ammonium salts, and finds that the stoicheiometric catalytic constant of the ammonium ion varies only between the limits 0·0386—0·0492, although the degree of dissociation of the salts (as judged by their conductivities) varied from 4% to 47%. It appears that in this reaction the association of the ammonium ion with various anions is closely paralleled by the association of the transition state with the same ions. It is intended to investigate other reactions in aqueous solution from the same point of view.

The most probable values for K_d derived above are $CaOH^+$ 0·051, $BaOH^+$ 0·23, TlOH 0·38. From a practical point of view it may be noted that for the range of ionic strengths which we have used the degrees of dissociation are well represented by the mean concentration dissociation constants K_c, as follows, $CaOH^+$ 0·11, $BaOH^+$ 0·43, TlOH 0·60. From a theoretical point of view it is of interest to see how far the observed constants can be accounted for by Coulomb forces between the constituent ions. By applying Bjerrum's treatment (*loc. cit.*) to our values of K_d we obtained the following values for the distance of closest approach of the ions : $CaOH^+$ 2·55 A., $BaOH^+$ 5·55 A., TlOH 1·23 A. The corresponding sums of the crystallographic radii are

$CaOH^+$ 2·52 A., $BaOH^+$ 2·88 A., TlOH 2·97 A. This shows clearly that an electrostatic explanation is adequate for the formation of $CaOH^+$ and $BaOH^+$, but that covalent forces must be involved in the formation of TlOH.

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