[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

# BASIC CATALYSIS IN THE DECOMPOSITION OF DIACETONE ALCOHOL

BY C. CLEMENT FRENCH

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## Introduction

In recent papers Åkerlöf[1] has presented the results of a careful study of the catalytic decomposition of diacetone alcohol by strong bases in aqueous solution, with and without added salt. This decomposition takes place according to the equation $C_6H_{12}O_2 \longrightarrow 2(CH_3)_2CO$. An attempt was made to explain the salt effect as a function of the individual ion activity of the hydroxyl ion. In the aqueous solutions of potassium, sodium and lithium hydroxides, in the absence of added salts, a direct proportionality was found between the activity of the hydroxide and the velocity of the reaction. As it appeared that this relation failed to remain valid below an hydroxide concentration of 0.1 *M*, measurements of the velocity in solutions of sodium and potassium hydroxides below this concentration have been carried out in order to determine what relation exists in the more dilute solutions.

In the study of the effect of salts on the rate of this decomposition, Åkerlöf used a 0.1 *M* alkali solution, with the concentration of added salt varying from 0 to 5 *M* at 0.5 *M* intervals. In connection with the investigation of the velocity in solutions of base more dilute than 0.1 *M*, it was thought advisable to examine the effect of a few salts in concentrations up to 1 *M*. The purpose of these experiments in the presence of neutral salts was to determine the salt effect in the region where the Brönsted theory predicts a linear salt effect and to determine whether the magnitude of the salt effect changes with change in the concentration of the catalyst.

The study by Åkerlöf[2] of the decomposition of diacetone alcohol by some amine bases suggested the possibility that this decomposition might be catalyzed by negative ions other than the hydroxyl ion. To test this possibility, a few experiments were made in phenol–sodium phenolate buffers.

## Experimental Method

The apparatus, as well as the experimental method used, was the same as that described by Åkerlöf in the papers mentioned above and does not require further discussion. Since the half time of all measurements reported here is greater than twenty minutes, there was always sufficient time available for the reacting solution to come to thermal equilibrium in

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[1] Åkerlöf, THIS JOURNAL, **48**, 3046 (1926); *ibid.*, **49**, 2955 (1927).

[2] Åkerlöf, *ibid.*, **50**, 733 (1928).

the thermostat before readings were begun. Consequently, in only a few cases were values of $k$ obtained showing a drift of more than 2%. In these cases the measurements were repeated with new solutions.

## Experimental Results and Discussion

**A. Aqueous Solutions of Potassium and Sodium Hydroxides.**—A summary of the measurements with these solutions is given in Table I. All concentrations are expressed in molality or moles of solute per 1000 g. of water. The diacetone alcohol was present in a concentration of about 0.15 $M$. Experiments were reproducible to within 2%. The velocity constants are expressed with the minute as the unit of time. All experiments were carried out at 25°.

TABLE I

DECOMPOSITION VELOCITY OF DIACETONE ALCOHOL IN SOLUTIONS OF POTASSIUM AND SODIUM HYDROXIDES

| | Potassium hydroxide | | Sodium hydroxide | |
|---|---|---|---|---|
| Molality, $M$ | $0.434\ k \times 10^4$ | $0.434\ k/M$ | $0.434\ k \times 10^4$ | $0.434\ k/M$ |
| 0.005 | 10.1 | 0.202 | ... | .. |
| .0100 | 20.3 | .203 | 20.1 | 0.201 |
| .0200 | 40.8 | .204 | 40.4 | .202 |
| .0400 | 83.3 | .208 | 82.7 | .206 |
| .0500 | 105.4 | .211 | 105.1 | .210 |
| .0655 | ... | .. | 134.0 | .204 |
| .0700 | 142.9 | .204 | ... | .. |
| .0755 | ... | .. | 156.4 | .202 |
| .0800 | 164.1 | .205 | ... | .. |
| .0850 | 173.9 | .204 | ... | .. |
| .100 | 208.0 | .208 | 205.0 | .205 |
| | (211.0)[a] | .. | (208.0)[a] | .. |
| | Average | .205 | Average | .204 |

[a] These values are taken from the paper of Åkerlöf, THIS JOURNAL, **49**, 2960 (1927), Table IV and show the agreement obtained.

In Fig. 1, $0.434\ k \times 10^4$, the observed velocity constant, has been plotted against the alkali hydroxide concentration. The figure shows that up to 0.1 $M$ base, the velocity is almost directly proportional to the hydroxide concentration. Also, from Table I it can be seen that the values of $0.434\ k/M$ deviate from the average value within the experimental error, and give a satisfactorily constant value for $0.434\ k/M$.

Åkerlöf[3] found that a close relationship existed between the activity of the hydroxide and the reaction velocity in solutions of sodium and potassium hydroxides above 0.2 $M$. For the concentration range from 0.2 to 2.0 $M$, the expression $\gamma M/K$, where $\gamma$ = the activity coefficient of the hydroxide, $M$ the molality of the hydroxide and $K$ the observed velocity constant, was a constant within the experimental error. A similar calculation has been carried out here to show how widely this expression deviates

[3] Åkerlöf, THIS JOURNAL, **49**, 2962 (1927).

from a constant value when the molality of the alkali hydroxide is 0.1 *M* or less. The results are shown in Table II. The activity coefficients were calculated from the equation

$$\log \gamma_{\text{MeOH}} = \frac{-0.354\sqrt{2m}}{1 + A\sqrt{2m}} + B2m - \log\left(1 + \frac{36m}{1000}\right)$$

where $\gamma$ is the activity coefficient, $A$ and $B$ are empirical constants and $m$ is the molal concentration of the base. The values of $A$ and $B$ are given in Table II and are those calculated by Harned and Åkerlöf.[4]

For values of $m$ above 0.2, the values of $\gamma M/0.434\ k \times 10^2$ for both sodium and potassium hydroxides remain constant.

The statement made by Harned and Åkerlöf[5] that this relation was probably not valid in the concentration range shown here is confirmed by the results in the table above. Therefore, it seems there is no doubt that in aqueous solutions of sodium and potassium hydroxides, below 0.2 *M* concentration, the decomposition velocity of diacetone alcohol is determined by the concentration of the hydroxide present and not by its activity. It is in this range of concentration that the activity of the alkali hydroxides is changing most rapidly, so that an agreement of the velocity with the change in activity of the hydroxide rather than with its concentration would show a marked deviation from the straight line relation in Fig. 1.

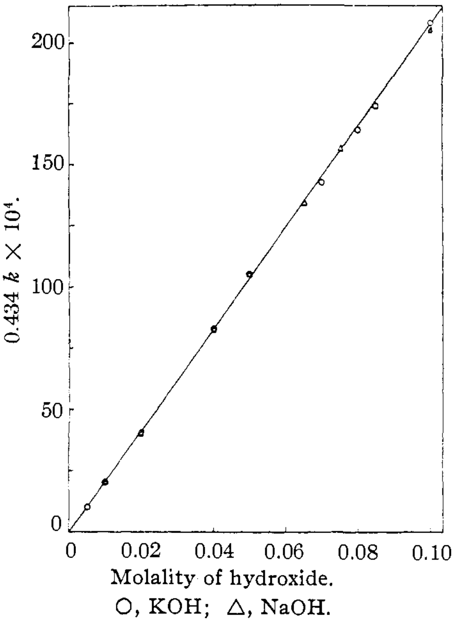

Fig. 1.—Effect of hydroxyl ion on the decomposition of diacetone alcohol.

According to the Brönsted theory, the velocity of a reaction of this type would be expressed by the equation

$$v = kc_{\text{A}}c_{\text{OH}^-}\frac{f_{\text{A}}f_{\text{OH}^-}}{f_{(\text{A, OH})^-}}$$

which in dilute solution would reduce to the simple equation

$$v = kc_{\text{A}}c_{\text{OH}^-}$$

since $f_{\text{A}}f_{\text{OH}^-}/f_{(\text{A, OH})^-}$ will equal unity. In the concentration range considered here, this simple equation appears to express correctly the decomposition rate.

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[4] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[5] Harned and Åkerlöf, *Trans. Faraday Soc.*, No. 90, **24**, Part 11, p. 676 (1928).

TABLE II

RELATION BETWEEN THE ACTIVITY OF THE HYDROXIDE PRESENT AND THE VELOCITY OF DECOMPOSITION OF DIACETONE ALCOHOL

| Molality of base, $M$ | Potassium hydroxide $\gamma$ | Potassium hydroxide $\frac{\gamma M}{0.434\,k} \times 10^2$ | Sodium hydroxide $\gamma$ | Sodium hydroxide $\frac{\gamma M}{0.434\,k} \times 10^2$ |
|---|---|---|---|---|
| 0.005 | 0.928 | 463 | .. | ... |
| .0100 | .903 | 444 | 0.902 | 448 |
| .0200 | .873 | 427 | .869 | 430 |
| .0400 | .836 | 401 | .830 | 401 |
| .0500 | .823 | 394 | .815 | 388 |
| .0655 | .. | ... | .798 | 391 |
| .0700 | .803 | 390 | .. | ... |
| .0775 | .. | ... | .786 | 390 |
| .0800 | .796 | 388 | .. | ... |
| .0850 | .792 | 386 | .. | ... |
| .100 | .783 | 376 | .767 | 374 |
| .200 | .745 | 371 | .716 | 366 |
| $A = 0.777$. $B = 0.0632$ | | | $A = 0.660$. $B = 0.050$ | |

As will be shown later, the spontaneous water reaction is entirely negligible here.

TABLE III

DECOMPOSITION OF DIACETONE ALCOHOL IN 0.050 $M$ SODIUM HYDROXIDE–SODIUM SALT SOLUTIONS

| Molality of added salt | Total equiv. salt concn. | $0.434\,k \times 10^4$ | $0.434\,k_2$ |
|---|---|---|---|
| Sodium Chloride | | | |
| 0 | 0.050 | 105.1 | 0.210 |
| 0.100 | .150 | 101.7 | .203 |
| .200 | .250 | 98.1 | .196 |
| .400 | .450 | 91.9 | .184 |
| .600 | .650 | 86.5 | .173 |
| .800 | .850 | 81.8 | .164 |
| 1.00 | 1.050 | 77.2 | .154 |
| Sodium Bromide | | | |
| 0.100 | 0.150 | 99.9 | 0.200 |
| .200 | .250 | 95.0 | .190 |
| .400 | .450 | 88.6 | .177 |
| .600 | .650 | 82.3 | .165 |
| .800 | .850 | 76.9 | .154 |
| 1.00 | 1.050 | 71.2 | .142 |
| Sodium Iodide | | | |
| 0.100 | 0.150 | 98.6 | 0.197 |
| .200 | .250 | 92.6 | .185 |
| .400 | .450 | 85.0 | .170 |
| .600 | .650 | 78.2 | .156 |
| .800 | .850 | 72.1 | .144 |
| 1.00 | 1.050 | 66.0 | .132 |

TABLE IV

DECOMPOSITION OF DIACETONE ALCOHOL IN 0.050 $M$ POTASSIUM HYDROXIDE–POTASSIUM SALT SOLUTIONS

| Molality of added salt | Total equiv. salt concn. | $0.434\,k \times 10^4$ | $0.434\,k_2$ |
|---|---|---|---|
| Potassium Chloride | | | |
| 0 | 0.050 | 105.4 | 0.211 |
| 0.100 | .150 | 102.0 | .204 |
| .200 | .250 | 98.5 | .197 |
| .400 | .450 | 93.0 | .186 |
| .600 | .650 | 89.3 | .179 |
| .800 | .850 | 86.4 | .173 |
| 1.00 | 1.050 | 84.2 | .168 |
| Potassium Bromide | | | |
| 0.100 | 0.150 | 100.3 | 0.201 |
| .200 | .250 | 95.5 | .191 |
| .400 | .450 | 88.7 | .177 |
| .600 | .650 | 84.2 | .168 |
| .800 | .850 | 81.1 | .162 |
| 1.00 | 1.050 | 77.2 | .154 |
| Potassium Iodide | | | |
| 0.100 | 0.150 | 98.5 | 0.197 |
| .200 | .250 | 92.5 | .185 |
| .400 | .450 | 85.0 | .170 |
| .600 | .650 | 78.8 | .158 |
| .800 | .850 | 74.2 | .148 |
| 1.00 | 1.050 | 69.8 | .140 |

**B. Alkali Hydroxide-Alkali Salt Solutions.**—These experiments were all carried out with an alkali hydroxide concentration of 0.05 *M* and with the added salt concentration varying from zero to one molal. Concentrations are all expressed in molality. All solutions were made up by weighing in a known quantity of standard alkali solution, then adding a sufficient weight of water to make the solution 0.05 *M*. To this solution was added the calculated weight of dried salt. Table III summarizes the results for the sodium salts in the presence of sodium hydroxide and Table IV those for the potassium hydroxide–potassium salt solutions. The velocity constants have been calculated with the minute as the unit of time. The temperature of all experiments was 25°.

The total equivalent salt concentration in Col. 3 is the sum of the molality of the base and the molality of the added salt.

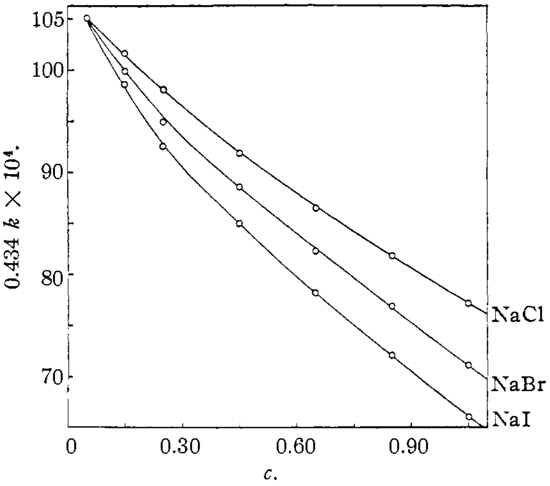


Fig. 2.—Effect of sodium salts on the decomposition of diacetone alcohol, $c = m_{\text{base}} + m_{\text{salt}}$.

The variation of the observed velocity constant, 0.434 $k$, with the total electrolyte concentration has been plotted in Fig. 2 for the sodium hydroxide–sodium salt solutions and in Fig. 3 for the potassium hydroxide–potassium salt solutions.

The fourth column in Tables II and III gives the observed velocity constant and the fifth column shows this constant divided by the concentration of hydroxyl ion, *i. e.*

$$k_2 = \frac{k_{\text{observed}}}{\text{molality of base}}$$

$k_2$ is then the molal velocity constant for the diacetone alcohol decomposition. In Fig. 4 0.434 $k_2$ is plotted against total electrolyte concentration (molality of base + molality of added salt) for the sodium hydroxide–sodium salt solutions and for the potassium hydroxide–potassium salt solutions, up to a total electrolyte concentration of 0.25 *M*. The salt effects of the base and of the added salt are taken as equal in the first approximation. The extent to which this approximation is incorrect may be judged from Fig. 4. Straight lines have been drawn through the various points at total electrolyte concentrations of 0.15 and 0.25 *M*, in such a way that all of these lines would meet at a point at zero electrolyte concentration. The two points at electrolyte concentration of 0.05 *M* represent the values for the bases in absence of added salt. The extent to which these points fail to lie on the various lines represents the error caused by assuming that the salt effect of the base and of the added salt will be equal. The smaller the concentration of the base in the total electrolyte concentration, the smaller will be the error introduced by this assumption, because the point on the plot for the base without added salt will be nearer the point of convergence of the various lines.

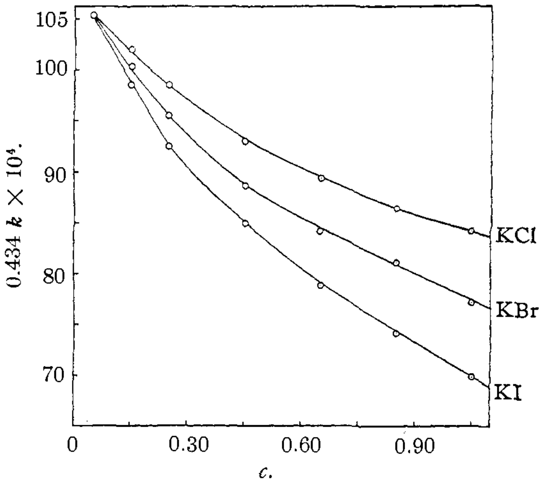


Fig. 3.—Effect of potassium salts on the decomposition of diacetone alcohol, $c = m_{\text{base}} + m_{\text{salt}}$.

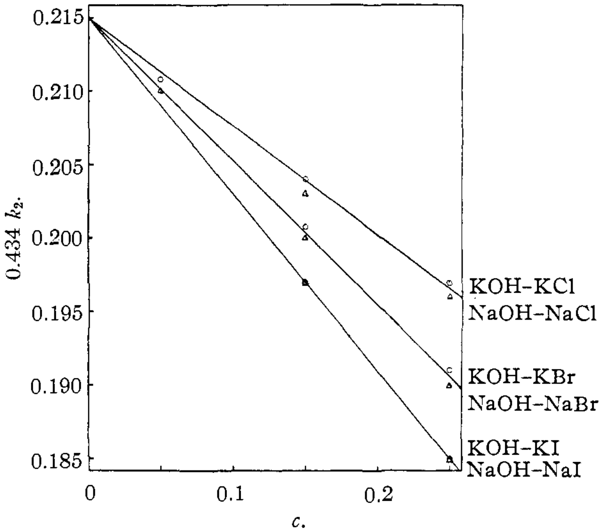
Above a total electrolyte concentration of 0.25 *M* the linear relationship which is found to exist in all six cases up to that concentration fails. For the concentration range below that value, the catalytic constant for diacetone alcohol in the various salt solutions may be represented by the following equations, where *m* is the total electrolyte concentration.

NaOH-NaCl, KOH-KCl $0.434\ k_2 = 0.215 - 0.074m$
NaOH-NaBr, KOH-KBr $0.434\ k_2 = 0.215 - 0.10m$
NaOH-NaI, KOH-KI $0.434\ k_2 = 0.215 - 0.12m$

From the above equations it is seen that the primary salt effect varies from about 3% for alkali chlorides to about 5.5% for alkali iodides.

Within the experimental error the equations for 0.434 $k_2$ depend upon the anion only.

In a consideration of the primary salt effect on the decomposition of nitrosotriacetone-amine, Kilpatrick[6] concluded that when the concentrations of the amine and of the salt were kept constant, and the hydroxyl ion concentration was varied, the salt effect was greater the lower the concentration of the hydroxyl ion. It is possible to test that conclusion for the diacetone alcohol reaction by a comparison of the results obtained here in 0.05 molal alkali solution, for given concentrations of added salts, with those obtained by Åkerlöf[7] for the same concentrations of added salts, but at 0.1 $M$ alkali concentration. Table V contains such a comparison at added salt concentrations of 0.5 and 1 $M$.



○, KOH-KX; △, NaOH-NaX.

Fig. 4.—Variation of molal velocity constant with total electrolyte concentration, $c = m_{\text{base}} + m_{\text{salt}}$.

The values in Cols. 2 and 3 of Table V represent the percentage decrease in velocity at the salt concentrations indicated, referred to the velocity in the base alone at the concentrations of base shown for the two columns.

The suggestion of Kilpatrick regarding nitrosotriacetone-amine, mentioned above, does not appear to hold for this reaction. The differences between the percentage decreases for the same concentration of added salt in the different concentrations of base are no greater than would be

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[6] Kilpatrick, THIS JOURNAL, **48**, 2091 (1926).

[7] Åkerlöf, *ibid.*, **48**, 3051 (1926), Tables II and III.

TABLE V

COMPARISON OF SALT EFFECTS ON DECOMPOSITION OF DIACETONE ALCOHOL AT DIFFERENT HYDROXYL ION CONCENTRATIONS

| Molality of added salt | Percentage salt effect in 0.1 $M$ base | Percentage salt effect in 0.05 $M$ base | Molality of added salt | Percentage salt effect in 0.1 $M$ base | Percentage salt effect in 0.05 $M$ base |
|---|---|---|---|---|---|
| 0.5 $M$ NaCl | 18.3 | 15.1 | 0.5 $M$ KCl | 13.3 | 13.5 |
| 1.0 $M$ NaCl | 28.4 | 26.5 | 1.0 $M$ KCl | 21.3 | 20.2 |
| 0.5 $M$ NaBr | 20.6 | 18.7 | 0.5 $M$ KBr | 15.6 | 16.8 |
| 1.0 $M$ NaBr | 31.2 | 32.2 | 1.0 $M$ KBr | 25.1 | 26.7 |
| 0.5 $M$ NaI | 24.5 | 21.7 | 0.5 $M$ KI | 20.4 | 22.2 |
| 1.0 $M$ NaI | 37.5 | 37.2 | 1.0 $M$ KI | 33.2 | 33.8 |

introduced by the experimental error of the original velocity constant determinations. While in solutions of a lower hydroxyl ion concentration such a difference might be noticeable, it does not appear to be true where the hydroxide concentration is as high as 0.05 $M$ or more.

**C. Phenol-Sodium Phenolate Buffer Solutions.**—Brönsted[8] defines a base as a substance which can take up hydrogen ions. Since the phenolate ion combines with a hydrogen ion to form phenol, it is a base by this definition, and a comparatively strong base since phenol is a weak acid. Consequently, it might be expected that the phenolate ion would decompose diacetone alcohol and an attempt was made to determine whether such was the case. Three buffer solutions were made up of phenol and sodium phenolate with the following concentrations: No. 1, 0.2 $N$ sodium phenolate and 0.2 $N$ phenol; No. 2, 0.15 $N$ sodium phenolate, 0.05 $N$ sodium chloride, 0.15 $N$ phenol; No. 3, 0.1 $N$ sodium phenolate, 0.1 $N$ sodium chloride, 0.1 $N$ phenol. All three had a total electrolyte concentration of 0.2 $N$ and a 1:1 ratio of phenol to sodium phenolate. The results are tabulated in Table VI.

TABLE VI

DECOMPOSITION OF DIACETONE ALCOHOL IN PHENOL-SODIUM PHENOLATE BUFFER SOLUTIONS

| Solution no. | 1 | 2 | 3 |
|---|---|---|---|
| $0.434\ k_{\text{observed}}$ | $2.06 \times 10^{-5}$ | $2.02 \times 10^{-5}$ | $2.00 \times 10^{-5}$ |

The apparatus used was not designed to measure accurately very slow reactions, and for reactions such as those recorded above, with half times in excess of twenty-one days, an experimentally observed infinity value could be very greatly in error. Therefore the graphical method suggested by Guggenheim[9] has been used to obtain the above values of $k$. While the accuracy obtainable in the rest of the work cannot be expected here, the results clearly indicate that any catalytic effect of the phenolate ion must be very small compared to the effect of the hydroxyl ion.

In all cases where catalytic effects by other acid molecules than hydrogen

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[8] Brönsted, *Chemical Reviews*, **5**, 286 (1928).

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

ions or by other basic molecules than hydroxyl ions, have been found, a water or spontaneous reaction has been found to occur.[10] Because of the slight catalytic effect of the phenolate ion, an attempt was made to determine the spontaneous reaction in the case of diacetone alcohol. The experiment was carried out in acid solution with a hydrogen-ion concentration of $1 \times 10^{-5}$ mole per liter in a sealed dilatometer of the type used by Brönsted, Kilpatrick and Kilpatrick.[11] The reaction was very slow, but from the calculation from the total volume change in a suitable experiment with sodium hydroxide, it was estimated that the velocity constant $0.434\ k$ was less than $3 \times 10^{-7}$ min.$^{-1}$. This corresponds to a half time of more than 800 days. With the very slight catalytic effect of the phenolate ion, a negligible water reaction was to be expected.

A calculation of the classical dissociation constant of phenol at 0.2 *M* salt concentration is possible from the results in buffer solutions. The hydroxyl ion concentration is obtained by dividing the observed velocity constant by the constant for molal hydroxyl ion at the same electrolyte concentration. In the absence of a specific linear equation for the salt effect of sodium phenolate, the molal constant has been calculated from the equation

$$0.434\ k_2 = 0.215 - 0.074m$$

which was found previously to serve for chlorides. This was chosen because sodium chloride was used as the salt in the buffer solutions to keep the constant total electrolyte concentration of 0.2 *M*. From this, we get

$$[\mathrm{OH}^-] = \frac{2.02 \times 10^{-5}}{0.200} = 1.01 \times 10^{-4} \text{ moles per liter}$$

using $2.02 \times 10^{-5}$ as the average of the observed values of $0.434\ k$ in Table VI. The concentration of hydrogen ions in the solution is then calculable from the relation

$$[\mathrm{H}^+] = K_w/[\mathrm{OH}^-]$$

Brönsted[12] predicted that the rapid decrease in the activity coefficients of the ions of a weak electrolyte must lead to an increase in the dissociation constant. Harned and others[13] have confirmed this prediction by the measurement of suitable cells and have calculated the dissociation constant of water in the presence of various alkali salts. If we take from the measurements mentioned a probable value at 0.2 *M* salt concentration of $1.95 \times 10^{-14}$ as the value for $K_w$, on the basis of $1.005 \times 10^{-14}$ for

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[10] Kilpatrick, THIS JOURNAL, **50**, 2891 (1928); Brönsted, *Proc. Faraday Soc.*, November (1928).

[11] Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

[12] Brönsted, *J. Chem. Soc.*, **119**, 574 (1921).

[13] Harned, THIS JOURNAL, **47**, 930 (1925); Harned and Swindells, *ibid.*, **48**, 126 (1926); Åkerlöf, *ibid.*, **48**, 1160 (1926); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); Harned, *Trans. Faraday Soc.*, No. 77, **23**, August (1927).

the value of $K_w$ in water of zero salt concentration, we can now calculate the H-ion concentration in our buffer solutions.

$$[H^+] = \frac{1.95 \times 10^{-14}}{1.01 \times 10^{-4}} = 1.93 \times 10^{-10} \text{ moles per liter}$$

Then the dissociation constant of the phenol in 0.2 $M$ salt solution can be calculated.

$$K_{\text{phenol}} = \frac{[H^+][\text{phenolate}^-]}{[\text{phenol}]} = [H^+] = 1.93 \times 10^{-10}$$

The value for the dissociation constant of phenol at 25° given in the literature is $1.09 \times 10^{-10}$.[14] This value was determined by conductance and refers to zero salt concentration. Since phenol is a weak electrolyte, its dissociation constant would be expected to increase in salt solution, as has been found here. The great extent to which $K_c$ varies with the salt concentration shows the necessity of stating the region of salt concentration in which the "constant" is to serve as the measure of acid or base strength. This same point has been shown in a study of secondary salt effects on the rate of decomposition of nitrosotriacetone-amine.[15] Consequently, values of $K_c$ determined by methods such as have been used here for the given salt concentrations at which they were determined, should be much better than values of $K_c$ which do not take this factor into consideration.

The decomposition of diacetone alcohol by other bases is being investigated and will be the subject of a later communication.

The author is indebted to Dr. and Mrs. Martin Kilpatrick, Jr., for the determination of the rate of the spontaneous decomposition of diacetone alcohol.

## Summary

1. The velocity of decomposition of diacetone alcohol in solutions of sodium and potassium hydroxides has been measured at 25°. The hydroxide concentration was decreased from 0.1 to 0.01 $M$ and it was found that over this range the velocity is proportional to the concentration of the hydroxide. The wide deviation from a rate proportional to the activity of the hydroxide has been shown.

2. The decomposition rate has been measured in 0.05 $M$ hydroxide solutions in the presence of various alkali salts. The molal velocity constant varies linearly with the total equivalent salt concentration up to a total concentration of 0.25 $M$, as predicted by the Brönsted theory. The linear equations obtained depend only on the anion of the salt present, when the cations of the base and the salt are the same. There appears to be no regular relation between the magnitude of the salt effect and the concentration of the catalyst.

[14] Lunden, *Z. physik. Chem.*, **70,** 249 (1910).

[15] Brönsted and King, THIS JOURNAL, **47,** 2530 (1925).

3. A few measurements were carried out with phenol–sodium phenolate buffer solutions to investigate the possibility of catalysis by the phenolate ion. If present, such catalysis must be quite small compared to the hydroxyl ion catalysis.

4. If this reaction has a spontaneous water reaction, its half time is greater than 800 days.

5. A value of $1.93 \times 10^{-10}$ for the dissociation constant of phenol in 0.2 molal salt solutions was calculated.

PHILADELPHIA, PENNSYLVANIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY]

# OXIDATION OF SELENIUM DIOXIDE AND OF TELLURIUM DIOXIDE WITH LEAD DIOXIDE[1]

BY FRANK C. MATHERS AND FRANK V. GRAHAM[2]

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## Introduction

DeCarli[3] tested the action of lead dioxide in the dry state upon several other oxides at temperatures varying from 250 to 300°. Barium, cuprous, stannous, ferrous, manganous, cobaltous and nickelous oxides reacted with the lead dioxide to form higher oxides. The lead dioxide was reduced to the monoxide. There was no evidence of reaction with calcium, cadmium, plumbous, zinc, magnesium, cupric, aluminum and titanium oxides. The less metallic oxides like arsenious, antimonous, chromium, molybdenum and tungsten reacted with the lead peroxide to form lead salts of the type of lead arsenate, lead antimonate, etc. He concluded that lead dioxide had a notable tendency to react with other oxides at relatively low temperatures.

This research was merely an extension of the above reaction to include selenium dioxide and tellurium dioxide, two oxides that had not been tried by DeCarli.

Lead selenate can be changed[4] easily to ammonium selenate. The ammonium selenate thus formed can be changed[5] into other selenates by crystallizing solutions of it with various metallic nitrates. The lead tellurate can be changed by sulfuric acid into telluric acid. There have been, heretofore, only indirect methods[6] of making lead selenate and lead

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[1] From the thesis for the degree of Master of Arts by Frank V. Graham at Indiana University, 1928.

[2] Professor of Chemistry, Ball State Teachers College, Muncie, Indiana.

[3] DeCarli, *Gazz. chim. ital.*, **56**, 55 (1926); *C. A.*, **20**, 1766 (1926).

[4] Mathers and Bonsib, THIS JOURNAL, **33**, 703 (1911).

[5] Unpublished work.

[6] (a) Becker, *Ann.*, **180**, 257 (1876); (b) Mathers, THIS JOURNAL, **30**, 1374 (1908); (c) Meyer and Moldenhauer, *Z. anorg. allgem. Chem.*, **116**, 193 (1921).