currence in these runs; consequently, each phase was worked up separately. Each was neutralized with solid sodium carbonate and extracted thrice with ether. The ether solutions were dried over anhydrous potassium carbonate, and that from the upper layer worked up according to (1), the one from the lower according to (2).

(1) Upon saturation of the extract with hydrogen chloride, di-4-morpholinehexane dihydrochloride precipitated; yield, 29.4 g (21.4%) after recrystallization from isopropyl alcohol; m. p. 261–261.5° (dec.). This material was found to be identical with that prepared from hexamethylene chloride and morpholine.

*Anal.* Calcd. for $C_{14}H_{30}O_2N_2Cl_2$: N, 8.50; Cl, 21.53. Found[10]: N, 8.62, 8.66; Cl, 21.37, 21.50.

The hydrochloride was converted to the free base with ammonium hydroxide. It melts at 40–42.5° (cor.).[11]

(2) The dried ether solution of the lower phase, when saturated with anhydrous hydrogen chloride, produced a dark viscous oil which, after three days in the refrigerator, finally solidified. After two recrystallizations, the product was dried *in vacuo* at 50° over phosphorus pentoxide; the ω-4-morpholinehexyl diphenylacetate hydrochloride weighed 17.8 g. (10.2%) and melted at 110.6–112.6° (cor.).

The ω-4-morpholinehexyl ester hydrochloride readily can be converted to the nitrate which is less soluble than the hydrochloride. A solution of 7.5 g. of the hydrochloride in 160 ml. of water was treated with 40 ml. of dilute nitric acid. The solution immediately became cloudy and crystals of the nitrate began to separate. These were collected after one-half hour and recrystallized from isopropyl alcohol, m. p. 119–120°, 7.1 g. or 90% yield.

*Anal.* Calcd. for $C_{24}H_{32}O_6N_2$: N, 6.30. Found[10]: N, 6.21, 6.28.

The nitrate will form a 4% aqueous solution when heated and allowed to cool; whereas, a 35% solution of the hydrochloride can easily be made.

## Summary

A study has been made of the preparation of ω-4-morpholinehexyl diphenylacetate. The intermediates, ω-hydroxyhexyl, ω-chlorohexyl and ω-bromohexyl diphenylacetate, have been prepared and identified.

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[11] Anderson and Pollard[4] found 35.5-38.5°.

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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, LOUISIANA STATE UNIVERSITY]

# The Diacetone Alcohol–Hydroxide Ion Reaction from the Standpoint of Ion-Dipole Theory

BY EDWARD S. AMIS, GEORGE JAFFÉ AND RALPH THEODORE OVERMAN[1]

The kinetic equation for reaction between ions and dipolar molecules

$$\ln k = \ln k_{\kappa=0} + \frac{\epsilon z_B \cos \vartheta_0}{DkTr_0^2} (\mu_0^* - \mu^* e^{-\kappa r_0} (1 + \kappa r_0)) \quad (1)$$

derived by Amis and Jaffé[1a] was tested as to the dependence of the reaction rate (between ions and dipolar molecules) both on ionic strength and on dielectric constant of the solvent using a positive ion reactant, namely, hydrogen ion. Since $\mu_0^* > \mu^* e^{-\kappa r_0} (1 + \kappa r_0)$ and since the term $\mu^* e^{-\kappa r_0} (1 + \kappa r_0)$ decreases at a decreasing rate while $\mu_0^*$ remains constant with increasing ionic strength, then for positive ionic reactants ($z_B$ positive) $k$ should increase with decreasing rate as the ionic strength is increased. For negative ionic reactants, however, $k$ should decrease with decreasing rate as ionic strength increases. Also $k$ should increase, but progressively less, with decreasing dielectric constant of the medium for positive ion reactants since, although the term $\mu_0^*/D$ increases, the smaller term $\mu^* e^{-\kappa r_0} (1 + \kappa r_0)$ decreases faster proportionally with decreasing diectric constant. For negative ionic reactants $k$ should decrease with decreasing rate as the dielectric constant is decreased.

For the hydrogen ion reacting with sucrose both in the presence and in the absence of salts, the predictions of Eq. (1) were fulfilled, as was the case also when hydrogen ion reacted with ethylene acetal in the absence of salts.[1a] The reaction between hydrogen ion and sucrose and that between hydrogen ion and glucose as a function of the dielectric constant of the media gave data in conformity with expectations.[1a]

It would be well, however, to test Eq. (1) using a *negative ion reactant* since there should not only be a change in the sign of the slope but also an inversion of the curvature of the empirical curves (ln $k$ *vs.* ionic strength and ln $k$ *vs.* $1/D^2$) if the equation correctly predicts the influences upon the rate constants of the ionic strength and dielectric constant of the medium.

Åkerlöf[2,3,4] has studied the rate of decomposition of diacetone alcohol by the hydroxide ion for various alkali metal hydroxides alone and in the presence of their uni-univalent and uni-bivalent salts. He has also studied the same reaction using sodium hydroxide in various mixed solvents. These data are ideal for testing Eq. (1).

In Fig. 1 we plot the data for the decomposition of diacetone alcohol in potassium hydroxide–uni-univalent potassium salt solutions of various ionic strengths. Also similar data for sodium hydroxide–uni-univalent sodium salt solutions are plotted in this figure. These data were plotted according to the suggestion of Amis and Jaffé[1a] who transformed Eq. (1) into the form

$$W = z^2/(1 + z + z^2/2 + (n^2/2D)(1 + z)) \quad (2)$$

by introducing the dimensionless variable

$$z = \kappa a = \kappa r_0 \quad (3)$$

and the dimensionless quantity

$$W = (\ln k - \ln k_{\kappa=0})(2DkTr_0^2)/\epsilon z_B \mu_0^* \cos \vartheta_0. \quad (4)$$

In Fig. 1 the solid line is the theoretical curve

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[1] Present address Louisiana College, Pineville, La.

[1a] Amis and Jaffé, *J. Chem. Phys.*, **10**, 598 (1942).

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

[3] Åkerlöf, *ibid.*, **49**, 2960 (1927).

[4] Åkerlöf, *ibid.*, **50**, 1272 (1928).

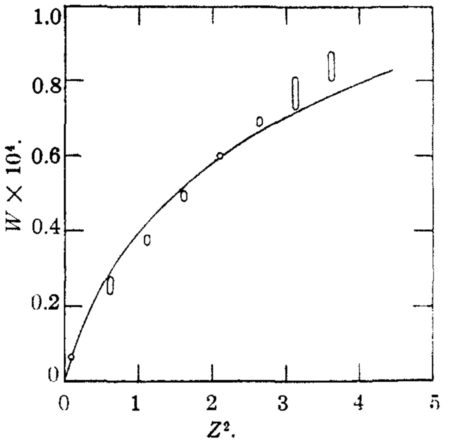

Fig. 1.—A plot of the specific rate constant *vs.* ionic strength for the decomposition of diacetone alcohol in the presence of potassium hydroxide–uni-univalent potassium salts and of like data in the presence of sodium hydroxide–uni-univalent sodium salts. The salts used with KOH were $KNO_2$, $KNO_3$, KCl, KBr, KI, KSCN and KCN. The salts used with NaOH were $NaNO_2$, $NaNO_3$, NaCl, NaBr, NaI, $NaClO_3$, NaSCN, and NaCN.

from Eq. (2) (neglecting the insignificant term $n^2/2D$), and the data for the seven potassium salts and the eight sodium salts fall within the length of the vertical ellipsoid at each specified value of $z^2$. The plot covers a range of ionic strengths from zero to 3.6. This is a very much wider range than is given for ion-ion reactions on the basis of the Debye–Hückel limiting law, but this range is used to give an idea of what range can be included in the theory. Table I contains the constants used in fitting the data to the theoretical curve in Fig. 1.

TABLE I

UNI-UNIVALENT SALTS

$r_0$ = 3.05 Å.; $\mu_0 = 4 \times 10^{-18}$

| Salt | $10^4 k_{\kappa=0}$ | $\mu_0 \times 10^{18}$ | $n^2$ |
|---|---|---|---|
| Potassium hydroxide–potassium salts | | | |
| $KNO_2$ | 212 | 6.15 | 1.08 |
| $KNO_3$ | 213 | 7.35 | 1.68 |
| KCl | 214 | 8.30 | 2.15 |
| KBr | 217 | 10.34 | 3.17 |
| KI | 222 | 14.6 | 5.30 |
| KCN | 215 | 8.79 | 2.40 |
| KSCN | 225 | 16.4 | 6.20 |
| Sodium hydroxide–sodium salts | | | |
| $NaNO_2$ | 209 | 10.04 | 3.02 |
| $NaNO_3$ | 210 | 10.60 | 3.30 |
| NaCl | 211 | 11.2 | 3.60 |
| NaBr | 213 | 13.4 | 4.70 |
| NaI | 217 | 17.5 | 6.78 |
| NaCN | 205 | 7.27 | 1.64 |
| NaSCN | 220 | 19.4 | 7.70 |
| $NaClO_3$ | 210 | 10.98 | 3.49 |

In general Åkerlöf[2] found the rate was slowed down to a less extent by a potassium salt than by the corresponding sodium salt at like concentrations. This is reflected in the smaller $\mu_0{}^*$ and $n^2$ values and the larger $k_{\kappa=0}$ values for the potassium salts. In the case of the cyanides the usual order of relative decrease of the rate was inverted for the potassium and sodium salts and here also the magnitudes of the constants for the two salts were inverted except for the magnitude of $k_{\kappa=0}$ which is larger for the potassium salt even in this case. The actual values of the constants correspond closely to the values used in fitting data for the positive hydrogen ion reactant to the theoretical curve.

Of all the salts studied by Åkerlöf, only potassium fluoride, potassium carbonate, sodium carbonate and sodium sulfate give data which do not conform to theory. Even in these cases the curvature of the log $k$–ionic strength data is that predicted by the theory, though the sign of the slope of the curve is upward with increasing ionic strength in opposition to what is to be expected from Eq. (1). Åkerlöf himself devotes special space to the discussion of these cases, but arrives at no definite conclusion as to the reason for their behavior. He does point out that the carbonate salts themselves promote the decomposition of diacetone alcohol and, furthermore, that they are hydrolyzed to give hydroxide ion, but even when full correction is made for the influence of hydrolysis still there is a marked increase of rate with increasing ionic strength in carbonate solutions. It is evident that these few salts do have specific effects upon the rate which is anomalous and cannot be accounted for on the basis of the present theory. It might be pointed out that the fluorides are abnormal in many of their properties.

In Fig. 2 a plot of the data for the reaction rate in solutions of alkali hydroxide–uni-bivalent alkali chromates is given to an ionic strength up to 13.6, since the data showed no marked departure from theory up to high values of ionic strength. In Table II the constants used in fitting these data to theory are recorded. Except for the values of $k_{\kappa=0}$, the relative magnitudes of the constants for the potassium and sodium chromates were in the same direction as for the majority of uni-univalent salts. This corresponds to potassium chromate slowing down the rate of reaction to a less extent than does sodium chromate for like concentrations of the two salts. The actual magnitudes of the constants agree very well with the values found for the uni-univalent salts.

TABLE II

UNI-BIVALENT SALTS

$r_0$ = 4.56 Å.; $\mu_0 = 4 \times 10^{-18}$

| Salt + Base | $10^4 k_{\kappa=0}$ | $\mu_0 \times 10^{18}$ | $n^2$ |
|---|---|---|---|
| $K_2CrO_4$ + KOH | 235 | 6.76 | 1.38 |
| $Na_2CrO_4$ + NaOH | 260 | 12.91 | 4.46 |

It might be pointed out that the value of the moment *in vacuo* of $\mu_0 = 4 \times 10^{-18}$ for diacetone alcohol was chosen as a reasonable value of this

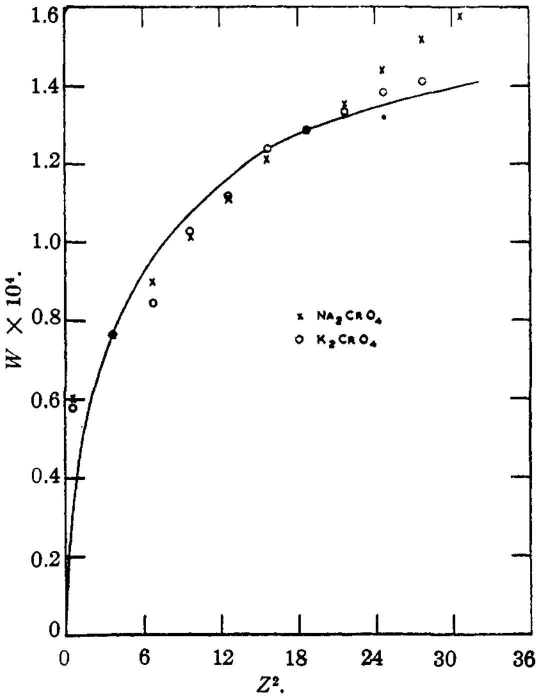

Fig. 2.—A plot of the specific rate constant *vs.* ionic strength for the decomposition of diacetone alcohol in the presence of KOH-$K_2CrO_4$ and of NaOH-$Na_2CrO_4$.

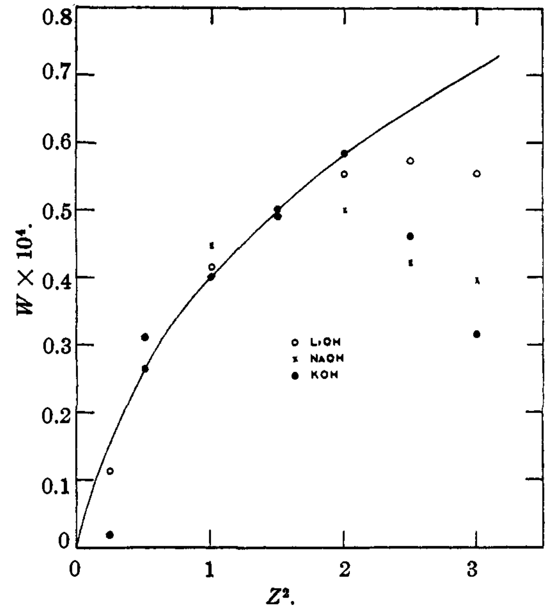

Fig. 3.—A plot of the specific rate constant *vs.* ionic strength for the decomposition of diacetone alcohol in the presence of different alkali metal hydroxides.

quantity since it could not be found in the literature. The values of the other constants are determined by trial and error after fixing the value of $\mu_0$.

Figure 3 is a plot of the data for the rate constants for the decomposition of diacetone alcohol in the alkali metal hydroxides of changing concentration. This plot extends only to an ionic strength of 1.2 and the data fit the theoretical curve reasonably well only to an ionic strength of about 0.8. The nature of the agreement is reminiscent of that for ion–ion reactions which generally fall off sharply from the limiting law at ionic strengths of roughly greater than 0.1. The lowest points for potassium and sodium hydroxides fall considerably below the theoretical curve. The reaction constants as measured would have to be 2.5 and 4% lower, respectively, than Åkerlöf's in order to fall on the theoretical curve. Åkerlöf's observation at 0.1 *N* NaOH, however, is confirmed by measurements of French, Murphy and Sturtevant[4a] who find *k* approximately constant at concentrations up to 0.1 *N*. (French's measurements extend from 0.005 to 0.1 normality, Murphy's from 0.01 to 0.1 and Sturtevant's from 0.03 to 0.095.) Thus, there seems to be a discrepancy between observation and theory at these low concentrations, unless the deviations are due to acid impurities as had been suggested to Sturtevant as a possible source of error. The values of the constants given in Table III show the increased effect of like concentrations of the hydroxides in reducing the rate as one goes from potassium hydroxide through sodium hydroxide to lithium hydroxide. The relative values of the constants for potassium hydroxide and sodium hydroxide are the same as in the majority of the corresponding alkali hydroxide–alkali uni-univalent salts.

TABLE III

UNI-UNIVALENT BASES

$r_0 = 4.82$ Å.; $\mu_0 = 4 \times 10^{-18}$

| Base | $10^4\ k_{\kappa=0}$ | $\mu_0 \times 10^{18}$ | $n$ |
|---|---|---|---|
| KOH | 212 | 5.20 | 0.606 |
| NaOH | 207 | 6.23 | 1.11 |
| LiOH | 208 | 10.0 | 3.00 |

To test the dependence of rate constants upon dielectric constants of the medium Amis and Jaffé[1a] made the following transformation of Eq. (1), setting

$$\kappa^2 = \lambda^2/D \tag{5}$$

$$\xi = \lambda a = \lambda r_0 \tag{6}$$

and

$$W' = (\ln k - \ln k_{\kappa=0})(2kT)/\xi z_B \mu^*{}_0 \lambda^2 \cos \vartheta_0 \tag{7}$$

the general relation

$$W' = (1/D^2)(1/(1 + \xi/D^{1/2} + \xi^2/2D)) \tag{8}$$

was obtained.

We give in Fig. 4 a plot of Åkerlöf's data for the decomposition of diacetone alcohol in 0.1 *N* sodium hydroxides when a mixed solvent was used. The data plotted are those for ethyl alcohol–water and *n*-propyl alcohol–water and are extended downward to a dielectric constant of 50. The constants are recorded in Table IV. The

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[4a] French, THIS JOURNAL, 51, 3215 (1929); Murphy, *ibid.*, 53, 477 (1931); Sturtevant, *ibid.*, 59, 1528 (1937).

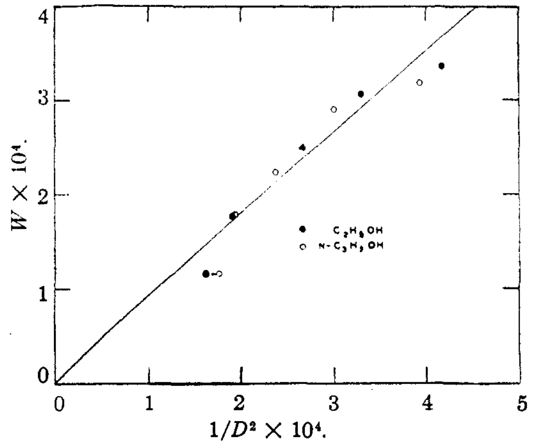

Fig. 4.—The specific rate constant *vs.* $1/D^2$ for the decomposition of diacetone alcohol in 0.1 *N* sodium hydroxide when mixed solvents were used.

values of these constants are fairly consistent with the values found for the ionic strength dependence and also with those determined by Amis and Jaffé for the dielectric constant dependence of rates involving a positive ionic reactant.

TABLE IV

MIXED SOLVENT

$r_0 = 1$ Å.; $\mu_0 = 4 \times 10^{-18}$

| Solvent | $10^4 k_{K=0}$ | $\mu_0 \times 10^{18}$ | $n^2$ |
|---|---|---|---|
| $C_2H_5OH-H_2O$ | 213 | 9.84 | 2.92 |
| $n$-$C_3H_7OH-H_2O$ | 219 | 23.9 | 9.95 |

The data for methyl alcohol, glycol and glycerol are in agreement with predictions in the direction and shape of the curve, but either $\mu_0$* and $n^2$ must be unreasonably large or $r_0$ must be unreasonably small to account for the great effect of these solvents in slowing down the rate. Amis and Cook[5] studying the dielectric and solvent effects upon the alkaline fading of brom phenol blue in glycerol-water mixtures found that the solvent had an abnormal effect upon the rate of this ion–ion reaction which was proportional to the amount of glycerol and could be accounted for upon the basis of the acidic nature of the glycerol, whereby the amount of hydroxide ion was effectively reduced. This explanation could account for the abnormal slowing down of the rate of decomposition of diacetone alcohol by alkali hydroxide in glycerol–water and glycol–water mixtures. However, the abnormal effect of methyl alcohol and of isopropyl alcohol, the latter of which actually increases the rate, must be attributed to specific solvent effects which are not yet clear. Such specific effects of solvent upon an ion-dipolar molecule reaction have been noted before.[6]

It should be pointed out that Eq. (5) of reference 1a is a very special case of Kirkwood's[7] solution for the potential of a particle with the most general charge distribution. Bateman, Church, Hughes, Ingold and Taher[8] arrive at an expression for the potential of a dipole which is exactly like that given by Eq. (5) mentioned above.

## Conclusions

1. Rate constants for the decomposition of diacetone alcohol in solutions of three alkaline hydroxides, alone and in the presence of seventeen alkali salts, were shown to agree with the theoretical equation proposed by Amis and Jaffé. The data gave not only a change in the sign of slope but also an inversion of the curvature of the empirical curves as predicted by theory.
2. Four alkali salts were found to give anomalous results which could not be explained either by Åkerlöf or by the authors.
3. The rate of this reaction in ethyl alcohol–water and $n$-propyl alcohol–water was found to agree reasonably well with theory. Here again there was the predicted change in sign of the slope and inversion of the curvature of the empirical curves.
4. Deviations of data from theory in the case of certain mixed solvents are discussed.

BATON ROUGE, LA. RECEIVED JULY 31, 1944

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(5) Amis and Cook, THIS JOURNAL, **63**, 2621 (1941).

(6) Amis and Holmes, *ibid.*, **63**, 2231 (1941).

(7) Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934). See also Scatchard and Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(8) Bateman, Church, Hughes, Ingold and Taher, *J. Chem. Soc.*, 979 (1940).