RESULTS OF MEASUREMENTS   (*Concluded*)

Substance	Number of detns.	Temp., °C.	L, in cal. per g.	Mean probable error	Observer
Dimethylaniline	5	192.7	87.48	±0.06	Wendt
Furan	4	31.2	95.50	± .02	Keenan
Furfuryl acetate	9	181.2	77.90	± .12	Maresh
Isoamyl bromide	3	121.6	57.84	± .30[b]	Fehlandt
Isopropyl bromide	3	58.6	55.19	± .09	Fehlandt
Isopropyl chloride	11	34.0	80.68	± .11	Wendt
Methyl amyl ketone	4	149.2	82.70	± .02	Keenan
Methylaniline	7	193.6	101.20	± .23	Wendt
Methyl furoate	8	181.8	84.18	± .13	Maresh
n-Propyl bromide	6	68.8	58.02	± .12	Wendt
n-Propyl chloride	4	45.7	84.32	± .26	Wendt
Tri-isobutylene	6	174.4	57.54	± .15	Maresh

[a] The smallness of the sample permitted only two runs; hence, 0.3 represents only deviation of each run from the mean. To calculate mean error by the method of least squares, at least three values are needed. [b] Some decomposition took place.

Summary

1.   The latest improvements in apparatus and procedure for the Mathews' electrical method of determining heats of vaporization have been given.

2.   The heats of vaporization of twenty-two compounds have been determined and their values stated.

MADISON, WISCONSIN

BASIC CATALYSIS IN THE DECOMPOSITION OF DIACETONE ALCOHOL

BY JOHN G. MILLER AND MARTIN KILPATRICK, JR.

In alkaline solution diacetone alcohol decomposes according to the equation $C_6H_{12}O_6 \longrightarrow 2(CH_3)_2CO$.   Koelichen[1] showed that for solutions originally containing less than 5% diacetone alcohol the equilibrium was so far displaced toward the acetone that the decomposition might be considered a monomolecular reaction proceeding to completion.   Furthermore, he found that for concentrations of alkali hydroxide below 0.1 N, the rate of reaction was proportional to the concentration of hydroxyl ion, and suggested that the reaction might be used to determine the dis-

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

sociation constants of weak bases. Åkerlöf[2] made a careful study of the decomposition by both strong and weak bases. From the rates of decomposition he evaluated, as will be shown later, the dissociation constants of a number of amines. More recently, French[3] showed the primary salt effect upon the reaction to be small, and again found proportionality, in dilute solution, between the rate of reaction and the hydroxyl-ion concentration.

At the suggestion of one of us (M. K., Jr.) French considered the possibility of the existence of catalysis by bases other than the hydroxyl ion. For the purpose of detecting possible catalysis by the phenolate ion he performed a number of experiments in phenol–sodium phenolate buffer solutions; these experiments showed that any catalytic effect of the phenolate ion was very small. We shall demonstrate that ammonia and the amines act as catalysts in the decomposition of diacetone alcohol, shall explain certain anomalies in the results of Åkerlöf, and shall re-evaluate the dissociation constants of a number of amines.

Experimental Method

The dilatometer designed by Åkerlöf was used in the present investigation. It was found desirable to force the reacting solution into the dilatometer under pressure rather than to draw it in by suction. The dilatometer was placed in a thermostat kept at $25 \pm 0.005°$.

Four bases were studied: ammonia, methyl-, dimethyl- and ethylamine. Buffer solutions of the ammonia–ammonium chloride type were formed by the addition of hydrochloric acid, and in each series of experiments the buffer solution was diluted with a sodium chloride solution of the same ionic strength. For the purpose of comparison with the data of Åkerlöf, concentrations have been expressed throughout in moles per 1000 grams of water as well as in molarities. The original diacetone alcohol concentration never exceeded 2% by volume of the reacting solution.

The velocity constants were calculated from the dilatometer readings by Guggenheim's[4] method, which is of particular advantage in the case of slow reactions such as these. The velocity constants are in terms of moles per 1000 grams of water, per minute.

Experimental Results and Discussion

In Table I and in Fig. 1 are given the results of the experiments in ammonia–ammonium chloride buffer solutions. The first four experiments, in which the acid–base ratio and the ionic strength remained constant,

2 Åkerlöf, THIS JOURNAL, 48, 3046 (1926); 49, 2955 (1927); 50, 733 (1928); 51, 984 (1929); Harned and Åkerlöf, Trans. Faraday Soc., No. 90, 24, 676 (1928).

3 French, THIS JOURNAL, 51, 3215 (1929).

4 Guggenheim, Phil. Mag., 1, 538 (1926).

TABLE I

EFFECT OF THE AMMONIA MOLECULE ON THE DECOMPOSITION OF DIACETONE ALCOHOL

Moles per liter of solution			Moles per 1000 g. of water			Ionic	$0.434\,k_{obs}.$
NH_3	NH_4Cl	NaCl	NH_3	NH_4Cl	NaCl	strength	$\times 10^6$
0.2200	0.0550	0.0000	0.2218	0.0554	0.0000	0.055	56.0
.1760	.0440	.0110	.1773	.0443	.0111	.055	46.9
.1100	.0275	.0275	.1105	.0276	.0276	.055	34.6
.0880	.0220	.0330	.0886	.0222	.0332	.055	31.2

Intercept $= 14.6 \times 10^{-6}$ $0.434\,k_{NH_3} = 185 \times 10^{-6}$

| .3756 | .0626 | .0000 | .3809 | .0634 | .0000 | .063 | 92.6 |
| .2255 | .0376 | .0219 | .2269 | .0378 | .0221 | .060 | 64.2 |

Intercept $= 22.2 \times 10^{-6}$ $0.434\,k_{NH_3} = 185 \times 10^{-6}$

comprise one series. They are represented by the lower line of Fig. 1. Since the spontaneous reaction (the decomposition in the absence of base) is negligible,[3] the intercept on the axis of velocity constants, 14.6×10^{-6}, gives the amount of the reaction due to the hydroxyl ion in these solutions.   The slope of the line gives 10^6 times $0.434\,k_{NH_3}$ the catalytic constant for molal ammonia at an ionic strength of 0.055.   In the last two experiments of Table I, represented by the higher line of Fig. 1, the acid–base ratio was smaller and the ionic strengths were somewhat different. These data show that the ammonia molecule markedly catalyzes the decomposition of diacetone alcohol.
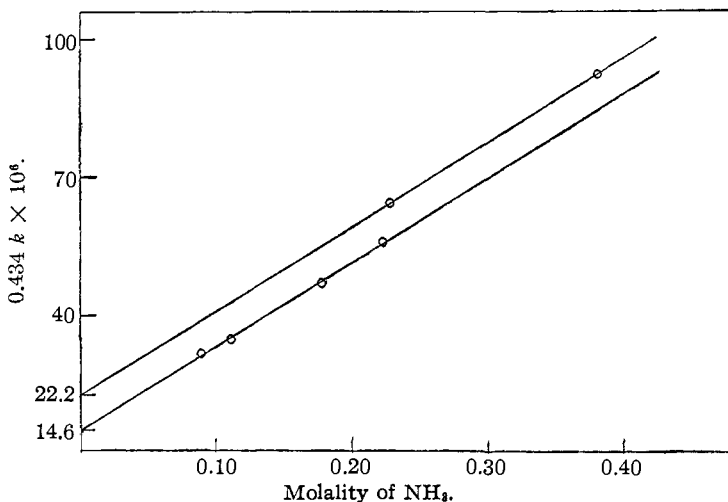

Fig. 1.—Effect of NH_3 molecule on the decomposition of diacetone alcohol.

Similarly, Tables II, III and IV and Figs. 2, 3 and 4 give the results obtained with the three amines.   There is in each case catalysis by the molecular base.   The catalytic constants stand in the order $k_{CH_3NH_2} > k_{C_2H_5NH_2} > k_{(CH_3)_2NH} > k_{NH_3}$.

TABLE II

EFFECT OF THE METHYLAMINE MOLECULE ON THE DECOMPOSITION OF DIACETONE ALCOHOL

Moles per liter of solution			Moles per 1000 g. of water			Ionic strength	$0.434\ k_{obs.}$ $\times\ 10^4$
CH₃NH₂	CH₃NH₃Cl	NaCl	CH₃NH₂	CH₃NH₃Cl	NaCl		
0.1650	0.0550	0.0000	0.1669	0.0556	0.0000	0.056	36.6
.1320	.0440	.0110	.1333	.0444	.0111	.056	30.8
.0825	.0275	.0275	.0830	.0277	.0277	.055	19.7

Intercept $= 4.0 \times 10^{-4}$ $0.434\ k_{CH_3NH_2} = 194 \times 10^{-4}$

TABLE III

EFFECT OF THE DIMETHYLAMINE MOLECULE ON THE DECOMPOSITION OF DIACETONE ALCOHOL

Moles per liter of solution			Moles per 1000 g. of water			Ionic strength	$0.434\ k_{obs.}$ $\times\ 10^5$
(CH₃)₂NH	(CH₃)₂NH₂Cl	NaCl	(CH₃)₂NH	(CH₃)₂NH₂Cl	NaCl		
0.1650	0.0550	0.0000	0.1683	0.0561	0.0000	0.056	76.2
.1320	.0440	.0110	.1341	.0447	.0112	.056	72.4
.0825	.0275	.0275	.0833	.0278	.0278	.056	59.5
.0660	.0220	.0330	.0666	.0222	.0333	.056	55.6

Intercept $= 42.5 \times 10^{-5}$ $0.434\ k_{(CH_3)_2NH} = 200 \times 10^{-5}$

TABLE IV

EFFECT OF THE C₂H₅NH₂ MOLECULE ON THE DECOMPOSITION OF DIACETONE ALCOHOL

Moles per liter of solution			Moles per 1000 g. of water			Ionic strength	$0.434\ k_{obs.}$ $\times\ 10^5$
C₂H₅NH₂	C₂H₅NH₃Cl	NaCl	C₂H₅NH₂	C₂H₅NH₃Cl	NaCl		
0.1650	0.0550	0.0000	0.1675	0.0559	0.0000	0.056	106.0
.1320	.0440	.0110	.1335	.0445	.0111	.056	92.7
.0825	.0275	.0275	.0832	.0277	.0277	.055	62.6
.0660	.0220	.0330	.0666	.0222	.0333	.056	55.2

Intercept $= 21.4 \times 10^{-5}$ $0.434\ k_{C_2H_5NH_2} = 504 \times 10^{-5}$

The classical dissociation constant of a weak base of the ammonia type may be written

$$K_B = \frac{c_{BH^+}c_{OH^-}}{c_B} \qquad (1)$$

In an aqueous solution of the base, without added acid

$$c_{OH^-} = \sqrt{K_B c_B}$$

and for a reaction catalyzed by the hydroxyl ion alone the velocity constant may be written

$$k_{obs.} = k_{OH^-}c_{OH^-} = k_{OH^-}\sqrt{K_B c_B} \qquad (2)$$

Whence for a series of weak bases B_1, B_2, B_3, . . . at constant stoichiometric concentration we have, neglecting the effect of formation of hydroxyl ion upon the concentration of base

$$k_1/k_2/k_3/\ldots = \sqrt{K_{B_1}}/\sqrt{K_{B_2}}/\sqrt{K_{B_3}}/\ldots \qquad (3)$$

the equation used by Åkerlöf.[5] Taking the dissociation constant of ammonia as standard Åkerlöf calculated from the velocity constants the dissociation constants of a number of amines.

⁵ Åkerlöf, THIS JOURNAL, **50**, 738 (1928).

We have found that

$$k_{obs.} = k_{OH^-}c_{OH^-} + k_Bc_B = k_{OH^-}\sqrt{K_Bc_B} + k_Bc_B \qquad (4)$$

For a series of weak bases at the same stoichiometric concentration, therefore

$$(k_1 - k_{B_1}c_{B_1})/(k_2 - k_{B_2}c_{B_2})/\ldots = \sqrt{K_{B_1}}/\sqrt{K_{B_2}}/\ldots \qquad (5)$$

We shall now use Åkerlöf's velocity constants and our values of the k's to recalculate, according to equation (5), the dissociation constants of methyl-, dimethyl- and ethylamine. Åkerlöf determined the velocity
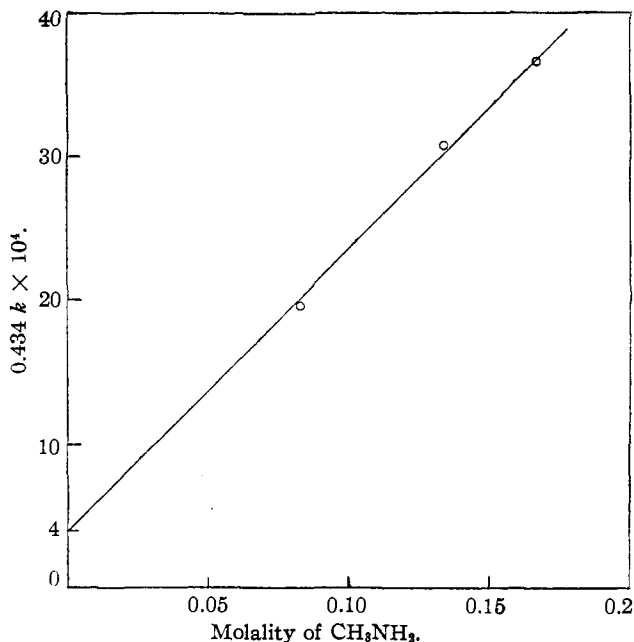

Fig. 2.—Effect of the CH_3NH_2 molecule on the decomposition
of diacetone alcohol.

constants for the decomposition of diacetone alcohol in 0.2 molal solutions of base. He took the dissociation constant of ammonia as 1.85×10^{-5} at 25°, a value obtained from conductivity measurements. We have assumed that the primary salt effect upon the decomposition of diacetone alcohol catalyzed by molecular base is small, i. e., we have set k_B for $\mu = 0$ equal to k_B for $\mu = 0.06$. From these data we have calculated by equation (5) the dissociation constants given in the third column of Table V.

Åkerlöf's values, and our recalculations from his data, are based upon measurements in unbuffered solutions of weak bases. It is desirable to use our own measurements to evaluate independently the dissociation constants of these bases. It has already been mentioned that, the spon-

TABLE V

DISSOCIATION CONSTANTS OF CERTAIN WEAK BASES AT 25°

Base	Åkerlöf[a]	Eq. 5	$K_B \times 10^4$ Eq. 6	Literature	
NH$_3$	..	..	0.175	0.179[b]	0.181[c]
CH$_3$NH$_2$	35.0	1.04	6.32	4.38[b]	5.00[d]
(CH$_3$)$_2$NH	9.7	8.5	6.7	5.2[b]	5.0[c]
C$_2$H$_5$NH$_2$	13.0	7.0	3.4	4.6[c]	5.6[d]

[a] Åkerlöf, THIS JOURNAL, **50**, 733 (1928). [b] Harned and Owen, *ibid.*, **52**, 5079 (1930). [c] "International Critical Tables," Vol. VI. [d] Bredig, *Z. physik. Chem.*, **13**, 289 (1894).

taneous reaction being negligible, the intercepts on the axis of velocity constants in Figs. 1, 2, 3 and 4 represent the amount of the reaction due
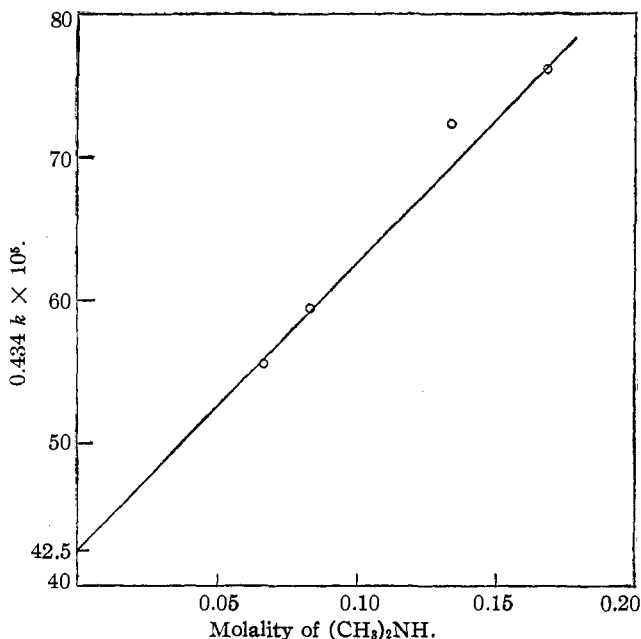

Fig. 3.—Effect of the (CH$_3$)$_2$NH molecule on the decomposition of diacetone alcohol.

to the hydroxyl ion, $k_{OH}\text{-}c_{OH^-}$. Representing the intercept by $k_{obs., OH^-}$ we have for the classical dissociation constant of the base

$$K_B = \frac{c_{BH^+}k_{obs., OH^-}}{c_B k_{OH^-}} \qquad (6)$$

Column 4 of Table V contains the values of K_B calculated by equation (6), using the buffer ratios and the intercepts given in Tables I, II, III and IV and using for the constant for molal hydroxyl ion at $\mu = 0.06$, French's figure 0.211. The fourth column of Table V gives the dissocia-

tion constants of the bases in question at an ionic strength of 0.06, in the presence of diacetone alcohol and acetone amounting to 2% of the volume of the solution, and in the presence of weak base at concentrations 0.4 to 0.07 molal.

A number of assumptions are involved in the calculation of the dissociation constants by equation (6). The taking of the intercept as the amount of the reaction due to the hydroxyl ion is justifiable only provided the dissociation constant of the weak base remains unchanged as the buffer is diluted with sodium chloride solution at constant ionic strength, and
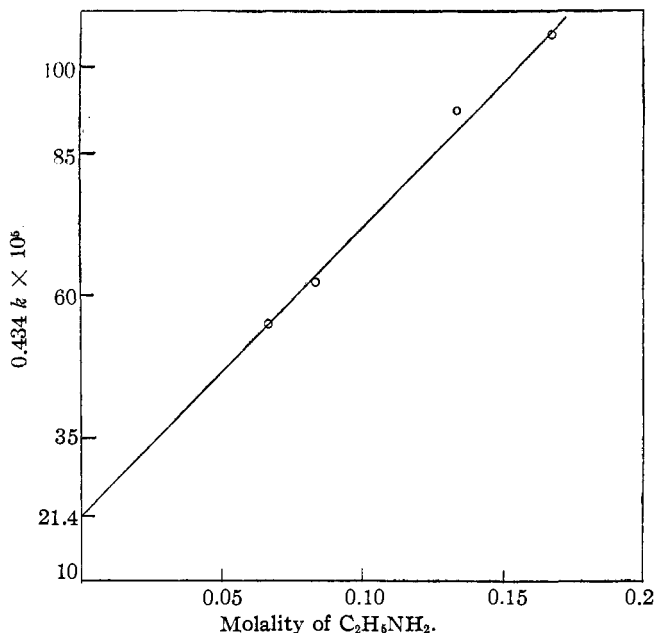

Fig. 4.—Effect of the $C_2H_5NH_2$ molecule on the decomposition of diacetone alcohol.

provided the solute effects on the decomposition of the diacetone alcohol catalyzed by the hydroxyl ion and by the molecular base remain unchanged during this dilution. Again, the use of French's figure 0.211 for the catalytic constant of molal hydroxyl ion at $\mu = 0.06$ is justifiable only provided the primary salt effect of the alkali hydroxides on the hydroxyl ion catalyzed reaction (this value was determined in solutions of sodium and potassium hydroxide) is the same as the solute effect of the constituents of the buffer solution.

The assumptions mentioned involve what may be described as "second order" salt effects—i. e., they deal with the substitution of one solvent salt for another. The primary salt effect on the decomposition cata-

lyzed by the hydroxyl ion is known to be small; from Table I the same conclusion might be drawn regarding the decomposition catalyzed by molecular base. It is believed that the errors resulting from the assumptions lie within the experimental error of the measurements.

In the last column of Table V are listed values of the dissociation constants of these bases taken from the literature. The values of Harned and Owen are based on electrometric measurements, the others upon measurements of conductivity. Columns 2 and 3 of Table V show that the correction of Åkerlöf's velocities for catalysis by the molecular base yields values of the dissociation constants in better agreement with those obtained by the electrometric and conductimetric methods. On the other hand, the values obtained from the velocities of decomposition of diacetone alcohol in the buffer solutions (column 4) are in even closer agreement.

The decomposition of diacetone alcohol adds another reaction to the list of those showing general basic catalysis as defined by Brönsted.[6] In most cases previously studied, it has been found that the catalytic constant increases with the basic strength, and that a roughly linear relationship exists between the logarithm of the catalytic constant and the logarithm of the constant of basic strength, which in terms of the dissociation constants used in this paper is K_B/K_W where K_W is the product of the ion concentrations of water. In the case of the present reaction, for the catalysts already studied—the hydroxyl ion, ammonia, and the three amines— no such linearity appears to exist. More catalysts must be investigated, however, before a generalization can be made.

Summary

1. The decomposition of diacetone alcohol is catalyzed by bases other than the hydroxyl ion. We have determined the catalytic constants for ammonia, and for methyl-, dimethyl- and ethylamine.

2. Taking into account catalysis by the molecular base, we have recalculated from Åkerlöf's data the dissociation constants of a number of weak bases and have obtained values in much closer agreement with those in the literature. We have also used our own measurements to determine the dissociation constants and have obtained values in good agreement with the literature.

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[6] Brönsted, *Chem. Reviews*, **5**, 286 (1928).