pressure of water when plotted in like manner. Through the temperature range 20 to 60°, a straight line with log p and $1/T$ as variables reproduces the experimental pressure values for either variety of water with error not in excess of 0.5%.

In Table II are shown values for relative pressures in systems A and B, in computing which we employed the ordinary water pressures found in "International Critical Tables,"[22] the deuterium water pressures of Miles and Menzies,[16] the pressures for system A given by Collins and Menzies[14] and the various pressures for system B as reported in Table I.

TABLE II

RELATIVE PRESSURES IN PERCENTAGE FOR SYSTEMS A AND B COMPUTED FROM DATA OF VARIOUS OBSERVERS

	A	B	B	B	B
T, °C.	C. and M.	M. and M.	S. and B.	Bell	P. and S.
20	30.5	32.4	29.2		
25	32.9	35.0	32.1	31.6	32.3
30	35.5	37.7	35.6	33.4	33.4
35	38.3	40.6		39.9	
39	40.6	43.0		41.7	
40	41.2	43.6	42.7		
50	47.6	50.3	50.5		
60	54.6	57.7	59.3		

These values are graphed in the manner described in Fig. 1, where we have added also our lines for the relative pressures in systems C and D.

If the modest extrapolation, which we have shown in Fig. 1, from the values of Partington and Stratton be allowable by reason of their utilization of four significant figures in expressing pressure, we can state that the relative pressure lines for system B as derived from the experimental data of all the other observers intersect the relative pressure line for system A as graphed in every case, contrary to our finding in this regard. It will be seen that, although it is true that the relative pressure lines of the other workers pass close to the same point at 25°, this is by no means the case at other temperatures.

Summary

Dissociation pressures in the systems consisting of deuterium water vapor and cupric sulfate penta- and trideuterate and also strontium chloride hexa- and dideuterate are reported in the temperature range 25 to 50°, and compared with analogous hydrate pressures. The related heat values are deduced and compared with those of others, and attention is called to certain discrepancies of our values from those obtained in three investigations by other workers.

PRINCETON, N. J. RECEIVED NOVEMBER 15, 1937

(22) "I. C. T.," Vol. III, 1926, p. 212.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO]

The Amine Catalysis of the Dealdolization of Diacetone Alcohol

BY F. H. WESTHEIMER AND HERZL COHEN

In their study of the dealdolization of diacetone alcohol catalyzed by amines, John Miller and Kilpatrick[1] observed that, at constant buffer ratio, the rate of the reaction increased with increasing buffer concentration. From this, they concluded that the aldol condensation is an example of general base catalysis, using these words in the sense defined by Brönsted.[2] Previously, however, French[3] had found that, in phenol–phenolate ion buffers, the rate is controlled by the hydroxyl ion concentration alone. The present work was undertaken to clear up this discrepancy.

For this purpose, the rate of the dealdolization of diacetone alcohol was measured in solutions buffered by methylamine and methylammonium chloride, by dimethylamine and dimethylammonium chloride, by trimethylamine and trimethylammonium chloride, and by triethylamine and triethylammonium chloride, all at 18° and at a constant ionic strength. The work of John Miller and Kilpatrick was verified and amplified with the first two amines. Molecular trimethylamine and molecular triethylamine, however, were found to be completely without effect on the rate of the reaction. The experimental results, together with the conclusions to be derived therefrom are presented in this paper.

Experimental

Apparatus and Method.—The rate of the reaction is easily and accurately measured dilatometrically.[4] The instrument employed was similar to that of Brönsted and

---

(1) John Miller and Kilpatrick, THIS JOURNAL, **53**, 3217 (1931).

(2) Brönsted, *Chem. Rev.*, **5**, 231 (1927).

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

(4) Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).

Guggenheim,[5] using mercury to seal the stopcocks. Since the half time of the reaction is great, the dilatometer was allowed to remain in the thermostat for an hour or more before readings were begun; thus a chamber for adjustment of temperature was not employed. The thermostat was maintained at 18.05 ± 0.001°. The velocity constants were calculated by the method of Guggenheim,[6] using decadic rather than natural logarithms.

Materials.—Eastman diacetone alcohol, freshly distilled for each run, boiled at 65–67° at 20 mm. Eastman methylamine hydrochloride was recrystallized from *n*-butyl alcohol.[7] Kahlbaum trimethylamine hydrochloride, when treated with 10 mole per cent. of sodium nitrite and hydrochloric acid, yielded no nitrosoamine on steam distillation. Commercial Solvents Company aqueous dimethylamine was converted into the hydrochloride. This salt was completely soluble in dry chloroform,[8] from which solvent it was crystallized by addition of acetone. In each case, the hydrochloride was treated with an excess of alkali, and the amine distilled into carbon dioxide-free water. Eastman triethylamine was fractionated with an eight-bulb column, and the fraction boiling at 88.7 to 89.0° at 755 mm. chosen. Mallinckrodt Analytical Reagent sodium chloride was used to maintain a constant ionic strength of 0.15.

Results

It had been shown previously that the reaction in the presence of alkali hydroxides is pseudounimolecular. The variations in k caused by a twenty-fold change in concentration of diacetone alcohol are only a few per cent., and would not invalidate this statement.[9] That this is also the case in the presence of amines is shown not only by the accuracy with which the data fit a first order equation but also by the fact that variation of the concentration of diacetone alcohol from 0.5 to 2%, keeping other factors constant, caused no appreciable change in the rate constant. A typical velocity run is recorded in Table I. While the average deviation was always of the order of a few tenths of a per cent., successive runs differed as much as 4%. Some wide deviations found in our early work were eliminated by scrupulous cleaning of the apparatus.

In the presence of the alkali hydroxides, acetone is the only product of the reaction. It would certainly be anticipated that the same would obtain in the presence of amines. As a final precaution, the following experiment was performed: a reaction mixture containing 0.15 molar methylamine, 0.15 molar methylammonium chloride and 5% diacetone alcohol was allowed to come to equilibrium. From a portion which had been neutralized, a 95% yield of pure acetone *p*-nitrophenylhydrazone was obtained.

TABLE I

A TYPICAL VELOCITY DETERMINATION

Run 9

0.05 *m* Methylamine
.0167 *m* Methylammonium chloride
.1333 *m* Sodium chloride
.080 *m* Diacetone alcohol

$\tau = 7$ hours

$k = 80.4\ 10^{-5}$ min.$^{-1}$

t, min.	v	v'	log $(v-v')$	log $(v-v')$ graph	Dev.
0	83.46	46.94	1.5625	1.5608	+0.0013
15	81.52	46.08	1.5495	1.5489	+ .0006
30	79.66	45.26	1.5366	1.5366	.0000
45	77.89	44.48	1.5239	1.5241	− .0002
65	75.60	43.42	1.5076	1.5082	− .0006
85	73.40	42.42	1.4911	1.4921	− .0010
135	68.32	40.05	1.4482	1.4520	− .0038
155	66.42	39.25	1.4341	1.4355	− .0014
175	64.64	38.42	1.4186	1.4190	− .0004
195	62.88	37.62	1.4024	1.4028	− .0004
225	60.38	36.50	1.3780	1.3790	− .0010
245	58.80	35.80	1.3617	1.3627	− .0010
265	57.25	35.05	1.3464	1.3464	.0000
285	55.74	34.39	1.3294	1.3301	− .0007
315	53.58	33.42	1.3045	1.3056	− .0011
				Average	0.0009 or 0.2%

With these fundamentals established, the rates of the reaction in the presence of the amine buffers can be considered. The rates were measured at three or more buffer concentrations, and, except for triethylamine, at two different buffer ratios, keeping the ionic strength constant. The slopes of the straight lines obtained by plotting the rate constant against amine concentration are the specific rate constants for the molecular amines, and were found independent of the concentrations of amine, substituted ammonium ion and hydroxyl ion. The intercept of these lines on the rate constant axis represents the part of the rate constant due to hydroxyl ion catalysis alone. The data are set forth graphically in Fig. 1 and analytically in Table II.

By demonstrating that the slope of the line in which ammonia concentration is plotted against rate constant, is independent of buffer ratio, Miller and Kilpatrick proved that the catalysis was due to molecular ammonia. The rate constant fitted the equation $k_{\text{obsd.}} = k_{\text{OH}^-}(\text{OH}^-) + k_{\text{B}}(\text{B})$. The results reported (Table II) show that, as they assumed, the same is true for methyl- and dimethylamine. The values of k_{B} are independent

---

(5) Brönsted and Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

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

(7) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 340.

(8) Knudesen, *Ber.*, **42**, 3994 (1909).

(9) Sturtevant, THIS JOURNAL, **59**, 1528 (1937).

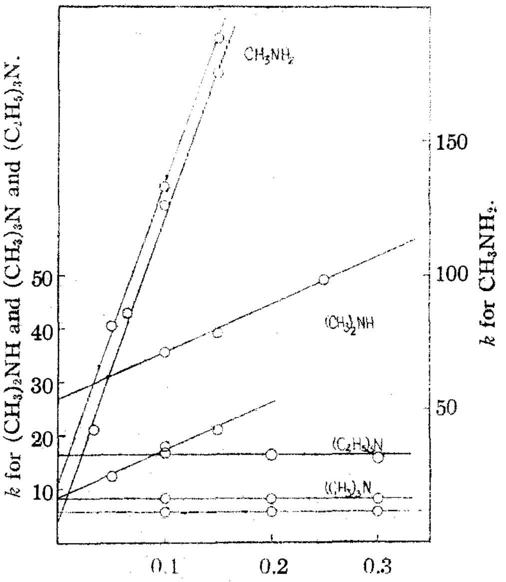


Fig. 1.

of the concentration of the amine, of the substituted ammonium salt and of hydroxide ions.

Table II

Amine Catalysis of the Dealdolization of Diacetone Alcohol

Concn. of amine	Concn. of substituted ammonium chloride	Concn. of NaCl	$k \times 10^{5}$[a] min.$^{-1}$	Specific rate constant $k_B \times 10^4$ mol.$^{-1}$ min.$^{-1}$
		Methylamine		
0.030	0.030	0.120	42.2	133
.065	.065	.085	86.0	
.100	.100	.050	126.0	
.150	.150	.000	175.0	
.050	.0167	.133	80.4	
.100	.0333	.117	133.0	
.150	.0500	.100	188.0	
		Dimethylamine		
0.050	0.050	0.100	12.4	8.8
.100	.100	.050	18.2	
.150	.150	.000	21.0	
.100	.0333	.117	35.7	
.150	.0500	.100	39.1	
.250	.0833	.067	49.2	
		Trimethylamine		
0.100	0.0143	0.136	5.71	0.00
.200	.0286	.121	5.88	
.300	.0429	.107	5.80	
.100	.0100	.140	8.08	
.200	.0200	.130	8.12	
.300	.0300	.120	8.13	
		Triethylamine		
0.100	0.050	0.100	17.1	0.00
.200	.100	.050	16.5	
.300	.150	.000	15.8	

[a] Some of these values are averages.

With trimethylamine, however, an entirely different situation obtains. Here the rate depends on the buffer ratio, but is independent of the buffer concentration. The unvarying rate is eloquent proof that the aldol condensation is not an example of general base catalysis. The rate depends on, and only on, the hydroxide ion concentration. 8.11 is the average rate constant for those buffers in which the ratio of concentration of amine to concentration of substituted ammonium chloride is ten. When the buffer ratio is seven, the average constant is 5.80. The hydroxide ion concentrations, then, stood in the ratio of 1 to 0.70, while the rate constant stood in the ratio of 1 to 0.72, a satisfactory agreement. Had there been a specific rate constant, due to molecular trimethylamine, as large as that due to ammonia (an even weaker base) the rate in the more concentrated buffers would have been almost double that in the more dilute.

The rate constants with triethylamine actually show a slight decrease with increasing buffer concentration. While the deviation is hardly greater than the experimental error, it may be real, for it is quite possible that the primary and secondary salt effects of the triethylammonium chloride and of sodium chloride are not identical.

Further, the absolute magnitude of the rates is that which would be expected if the catalysis were due only to hydroxide ions. Dividing the observed rate by the catalytic constant for hydroxide ions (0.107), the hydroxide ion concentration of the solution is obtained. From this and the buffer ratio, the dissociation constant of the amine can be estimated.

The most accurate determination of the dissociation constant of the methyl amines was made at 25° by Harned and Owen.[10] Further, Harned and Robinson[11] have determined the activity coefficients of these amines in the presence of sodium chloride, again at 25°. Assuming that the difference, in both the primary and secondary salt effects, between sodium chloride and a tertiary ammonium chloride is negligible, and that the activity coefficients at 25° do not differ appreciably from those at 18°, 3.2×10^{-5} is calculated as the true value for the dissociation constant of trimethylamine at 18°. Harned and Owen's value at 25° is 5.45×10^{-5}. Considering the assumptions involved and the difference in temperature,

---

(10) Harned and Owen, This Journal, **52**, 5079 (1930).

(11) Harned and Robinson, *ibid.*, **50**, 3157 (1928).

the agreement is satisfactory, and the conclusion is strengthened that, in trimethylamine–trimethylammonium chloride buffers, the rate is determined by the OH^- concentration alone.

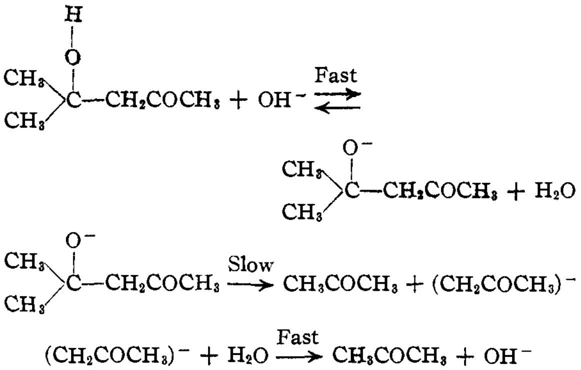
A similar calculation of the dissociation constant of triethylamine involves the additional assumption that the activity coefficients for triethylamine do not differ appreciably from those of trimethylamine. The value obtained from our data is 3.2×10^{-4}. Previous investigators[12] have found 6.4×10^{4} and 5.65×10^{-4} for the dissociation constant of triethylamine; their values are not, however, corrected by the use of activity coefficients.

Likewise, following John Miller and Kilpatrick we can determine the dissociation constants of methyl- and dimethylamines from the intercepts on the rate constant axis of the plots of rate against buffer concentration. The value thus obtained for methylamine is 3.2×10^{-4}, and for dimethylamine 3.4×10^{-4}. The corresponding constants as given by Harned and Owen are 4.38×10^{-4} and 5.26×10^{-4}. Again considering the difference in temperature, the assumptions already cited, and the errors of extrapolation, the agreement is as good as could be expected.

Discussion

The results of this investigation confirm those of Miller and Kilpatrick insofar as they show that the rate of the dealdolization of diacetone alcohol, catalyzed by methyl- and dimethylamine, is the sum of an hydroxyl ion catalysis and a catalysis due to molecular amine. Molecular trimethyl- and triethylamines, however, do not affect the rate, nor, according to French, does phenolate ion. We are then forced to the conclusion that this is not a case of general base catalysis. It is illuminating to discuss the mechanism of the aldol condensation in the light of these results.

The accepted theory of the aldol condensation[13] would demand that the dealdolization of diacetone alcohol take place in the following steps: first, a proton would be lost from the alcohol group of the aldol. Next, this ion would decompose to acetone and the enolate ion of acetone. The latter would then acquire a proton from the solvent. Since, as has been shown above, the reaction is not general base catalyzed, we are justified in concluding that the time consuming step is not the removal of the proton, but that the alcoholate ion exists in equilibrium with aldol. The slow reaction is the unimolecular decomposition of the alcoholate ion. Neglecting the reverse reaction, these steps are outlined below



$$(CH_3)_2C(OH)CH_2COCH_3 + OH^- \overset{\text{Fast}}{\rightleftarrows} (CH_3)_2C(O^-)CH_2COCH_3 + H_2O$$

$$(CH_3)_2C(O^-)CH_2COCH_3 \xrightarrow{\text{Slow}} CH_3COCH_3 + (CH_2COCH_3)^-$$

$$(CH_2COCH_3)^- + H_2O \xrightarrow{\text{Fast}} CH_3COCH_3 + OH^-$$

Since the concentration of the ionized aldol would be low, the rate of the reaction should vary with the hydroxyl ion concentration, as observed. That the reaction in no way involves the enolization of the aldol has long been known, since isobutraldol easily reverts to isobutraldehyde.[14]

There remains, however, the question of why some amines catalyze the reaction. From the data presented here, a possible hypothesis is that a necessary (but probably not a sufficient) condition for catalysis by molecular amines is the presence of at least one hydrogen atom attached to the amine nitrogen. Since the rate varies linearly with the amine concentration, it is apparent that an intermediate in the reaction must be a compound formed between the aldol and the amine, and according to this theory, involving the amine hydrogen. A substituted ketone ammonia (hydrated ketimine) would satisfy the kinetic requirements.

The idea of a ketimine as intermediate in condensations similar to the aldol is not new.[15] Qualitative differences in behavior between primary and tertiary amines have been noted before.[16] Compounds have even been isolated which contained the aldehyde, amine, and, for example, nitroparaffin.[17] But it is difficult to establish, without kinetic evidence, that these com-

---

[12] Bredig, *Z. physik. Chem.*, **13**, 191 (1894); Hall and Conant, THIS JOURNAL, **49**, 3047 (1927).

[13] Hückel, "Theoretische Grundlagen der organischen Chemie," 2nd ed., Vol. I, Akademische Verlagsgesellschaft, Leipzig, Germany, 1934, p. 188.

[14] Usherwood, *J. Chem. Soc.*, **123**, 1717 (1923).

[15] Knoevenagel, *Ber.*, **31**, 2596 (1899).

[16] Knoevenagel, *Ann.*, **281**, 25 (1894); Worrall, THIS JOURNAL, **56**, 1556 (1934).

[17] Cerf, *Compt. rend.*, **195**, 1084 (1932).

pounds are intermediates, and not the products of a side reaction, in equilibrium with the starting or final products, but not directly concerned in the conversion of the ones to the others.

The data here presented indicate the existence of the ketone amine intermediate, but do not settle the question of its structure, or why it should decompose rapidly with respect to diacetone alcohol. In fact, a mechanism which would depend upon the concentrations of the substituted ammonium ion and hydroxide ion would be indistinguishable kinetically from one depending on the concentration of the amine.

The authors wish to thank Professor M. S. Kharasch for his helpful suggestions during the course of this work.

Summary

1. The rate of the dealdolization of diacetone alcohol has been measured in buffered solutions containing methyl-, dimethyl-, trimethyl- and triethylamine, at several buffer concentrations and buffer ratios.

2. While molecular methyl- and dimethylamine catalyze the reaction, molecular trimethylamine and molecular triethylamine are without effect.

3. It is concluded therefore that the aldol condensation is not an example of general base catalysis.

4. The mechanism of the reaction, in the presence and the absence of amines, is discussed.

CHICAGO, ILL. RECEIVED AUGUST 26, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Cleavage of Diphenyl Ethers by Sodium in Liquid Ammonia. III. 4,4'-Disubstituted Diphenyl Ethers[1]

BY FRED C. WEBER AND FRANK J. SOWA

It has been shown[2] that a solution of sodium in liquid ammonia reacts vigorously and quantitatively with substituted diphenyl ethers. The products formed are substituted benzenes and phenols. The substituted phenols alone were determined experimentally and it was observed that the relative proportions of the two possible cleavage products formed in each reaction vary with the nature of the substituents in the phenyl nucleus. It was pointed out that the electron is probably the effective cleavage reagent, since sodium amide in liquid ammonia does not cleave diphenyl ether, thus eliminating the possibility of the sodium ion being the effective reagent.

The purpose of this investigation was to determine the effect of various substituents on the manner in which 4,4'-disubstituted diphenyl ethers are cleaved by sodium in liquid ammonia, the method having especial merit because one can make a comparison of the effect of two dissimilar groups within the same molecule.

Experimental

A standard method of cleavage of the diphenyl ethers, outlined in the first article of this series,[2] was used throughout this work. The cleavage products were extracted with ether or benzene and then fractionated using an efficient Widmer column.

TABLE I

PHYSICAL PROPERTIES OF THE DIPHENYL ETHERS PREPARED

No.	Compds. $R—C_6H_4—O—C_6H_4—R'$ R	R'	B. p. at indicated press. °C.	Mm.	M. p., °C.
1	*p*-Methyl	*p'*-Methoxy[a]	193–198	22	49–50
2	*p*-Methyl	*p'*-Nitro	223–227	25	65
3	*p*-Methyl	*p'*-Amino	195–199	16	119
4	*p*-Methoxy	*p'*-Nitro	218–222	16	106–7.5
5	*p*-Methoxy	*p'*-Amino	191–192	4	75–6.5
6	*p*-Methoxy	*p'*-Hydroxy[a]	189–193	16	64–5
7	*p*-Methyl	*p'*-*t*-Butyl[a]	174–178	4	*b*

[a] Compounds previously unreported in the literature.

[b] n^{25}_D 1.5488, sp. gr.$_{25}$ 0.9898.

Compounds nos. (2) and (4) were prepared according to the method of Brewster and Groening, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. XIV, p. 67; nos. (3) and (5) by reduction of the corresponding nitro compounds employing the method of Suter, THIS JOURNAL, **51**, 2538 (1929); nos. (1), (6) and (7) were prepared using the method described by Sartoretto and Sowa.[2] All of the diphenyl ethers described in this paper were purified by distillation under reduced pressure.

The cleavages of all of the diphenyl ethers studied, with the exception of the 4-methoxy-4'-hydroxydiphenyl ether, require two atom equiva-

---

[1] Original manuscript received July 6, 1937. For previous article see Kranzfelder, Verbanc and Sowa, THIS JOURNAL, **59**, 1488 (1937).

[2] Sartoretto and Sowa, *ibid.*, **59**, 603 (1937).