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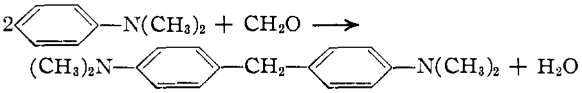
Kinetics of the Condensation of Dimethylaniline with Formaldehyde

BY YOSHIRO OGATA[1] AND MASAYA OKANO

The condensation of dimethylaniline (abbreviated as DMA in this paper) with formaldehyde (FA) which leads to *p,p'*-tetramethyldiaminodiphenylmethane (TMD), an important intermediate in the preparation of the di- and triphenylmethane dyestuffs



seems to have been scarcely studied from the kinetic standpoint. Smith and Welch[2] observed that *p*-dimethylaminobenzyl alcohol (DB) condensed with DMA in the presence of hydrochloric acid forming TMD, and that the rate of its formation was much faster than that from DMA and FA by comparing the color of the oxidation product of TMD. The work reported in this paper summarizes the results obtained on the kinetic study of the reaction carried out by the estimation of the formaldehyde unreacted.

Experimental

Materials.—Commercial DMA was freed from aniline, monomethylaniline and water in the successive distillation, boiling with acetic anhydride, distillation, stirring with a solution of sodium hydroxide, drying over potassium hydroxide, and final distillation, and it boiled constantly at 192.5°. The formaldehyde was of the best quality. The trace of formic acid contained in it had no influence on the estimation. *p*-Dimethylaminobenzyl alcohol was prepared according to Smith and Welch.[3] It boiled at 165° (4 mm.).

Apparatus and General Procedure.—The apparatus was substantially as already described in the study of the hydrolysis of nitriles,[4] *i. e.*, a three-necked flask, fitted with a thermometer, a reflux condenser, and a tube into which air could be blown for pushing out the sample, was used. The flask was immersed in a water-bath, the temperature of which was maintained to less than ±0.5° by using a gas temperature-regulator.

Two hundred cc. of aqueous solution of DMA hydrochloride (or sulfate) (prepared by dissolving a weighed amount of DMA in the acid solution) in one vessel and 100 cc. of aqueous FA solution in the other were heated until temperature equilibrium was reached. The two solutions were then mixed, the 20-cc. aliquots were taken out at known intervals of time, and the amount of FA remaining in the solution was determined by the sulfite method.[5] The sample was poured into 50 cc. of cold water to stop the further reaction, neutralized with sodium hydroxide solution after adding 3–4 drops of 1% rosolic acid solution as an indicator, and finally added with 25 cc. of 0.5 *N* sodium sulfite solution. After the solution had stood for a half-hour, the freed sodium hydroxide was titrated with 0.1 *N* hydrochloric acid to the point of the complete disappearance of the red color.

Results and Calculations.—The effects of *p*H, the addition of salts, and the molar ratio of DMA to FA upon the rate are shown in Table I. The rate constants k(l./sec. mole) and their probable errors were calculated by means of the following equations which were deduced from equation (7) described in the paragraph Discussion of Results. If $d \neq 2f$

$$k = \frac{1}{t(d - 2f)} \ln \frac{f(d - 2x)}{d(f - x)}$$

and if $d = 2f$

$$k = \frac{1}{2t}\left(\frac{1}{f - x} - \frac{1}{f}\right)$$

Here, d and f are the initial concentrations of DMA and FA in moles/l., respectively, and x the consumed FA in moles/l. after t seconds. The values of *p*H in the reaction mixtures were measured at 30° by the glass electrode method.[6]

TABLE I

RATES OF THE ACID-CATALYZED REACTION OF DIMETHYLANILINE WITH FORMALDEHYDE (0.10 *M*). TEMP. 80.0 ± 0.5°, CONCENTRATION IN MOLES/L.

No.	DMA, m./l.	Acid, m./l.	Salt, m./l.	$k \times 10^4$ [a]	*p*H
			HCl-catalyzed		
1	0.20	0.40	None	0.83 ± 0.02	0.7
2	.20	.25	None	1.29 ± .03	1.4
3	.20	.20	None	1.86 ± .02	2.9
4	.20	.20	NaCl, 0.50	2.51 ± .04	2.9
5	.20	.20	NaCl, 1.00	3.12 ± .04	3.0
6	.20	.20	NaCl, 3.00	5.8 ± .1	3.1
7	.20	.20	KCl, 3.00	6.1 ± .1	3.2
8	.10	.10	None	0.78 ± .02	2.9
9	.15	.15	None	1.32 ± .02	2.9
10	.25	.25	None	2.40 ± .03	2.9
11	.30	.30	None	3.04 ± .03	2.9
			H_2SO_4-catalyzed		
12	0.20	0.20	None	2.12 ± 0.03	1.2
13	.20	.125	None	3.95 ± .05	1.8
14	.20	.10	None	5.2 ± .1	3.0
15	.20	.10	Na_2SO_4, 0.25	7.4 ± .1	3.2
16	.20	.10	K_2SO_4, 0.25	7.5 ± .1	3.2
17	.10	.05	None	2.17 ± .02	3.0
18	.15	.075	None	3.89 ± .03	3.0
19	.25	.125	None	7.0 ± .1	3.0
20	.30	.15	None	8.7 ± .1	3.0

[a] Figures following ± show probable errors.

Some Qualitative and Complementary Experiments.—The problem of rate-determining step had been solved by Smith and Welch,[2] who recognized that DMA and DB reacted faster than DMA

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[2] Smith and Welch, *J. Chem. Soc.*, 1136 (1934).

[3] Smith and Welch, *ibid.*, 730 (1934).

[4] Ogata and Okano, *J. Chem. Soc. Japan*, **70**, 33 (1949).

[5] Lemme, *Chem. Ztg.*, **27**, 896 (1903); Doby, *Z. angew. Chem.*, **20**, 354 (1907); Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1944, pp. 257.

[6] The authors are grateful to instructor Tomota Nishi in Professor Okada's electrochemical laboratory of Kyoto University for his kind assistance in measuring *p*H.

and FA. We also confirmed the phenomenon in comparing microscopically the rates of crystallization of TMD under the same conditions. Moreover it was observed that the reaction of DMA and DB is much accelerated by acid. The possibility of the decomposition of DB into DMA and FA by adding acids or by heating was denied, since no aldehyde was detected with the Schiff reagent. The facts, observed above, agree with the mechanism which involves the slow irreversible formation of $p\text{-}(CH_3)_2NC_6H_4{}^+CH_2$ from DMA and the conjugate acid of FA, followed by the rapid condensation of the product with a second molecule of DMA (see equation (4) and (5)).

The rate and the salt effect in the neutral medium were studied in the following experiments. Into a 300-cc. flask, equipped with an air-tight stirrer, was introduced 100 cc. of FA solution (concentration, 0.5 mole/l.). To the solution was added 0.1 mole of DMA, emulsified through vigorous agitation (600 r. p. m.), and heated at 90 ± 1° for four hours. The consumption of FA was measured after suitable time intervals and the amount of TMD produced was roughly estimated. The results showed that the consumed FA after four hours was only 4% and the isolation of TMD difficult. But by adding 0.3 mole of sodium chloride to the solution, the consumption became 28% and 3.0 g. of TMD was isolated in crystals (identified in the mixed melting point test). In the same way, by the addition of 0.15 mole of anhydrous sodium sulfate, the consumption was raised to 8% and 0.8 g. of TMD was obtained. Therefore, some catalytic action of salts would probably be present.

Discussion of Results

The results obtained above imply the reaction mechanism

$$C_6H_5N(CH_3)_2 + HCl \rightleftarrows C_6H_5N(CH_3)_2HCl \quad (1)$$

$$C_6H_5N(CH_3)_2HCl \rightleftarrows C_6H_5N^+(CH_3)_2H + Cl^- \quad (2)$$

$$CH_2O + H_3O^+ \rightleftarrows \overset{+}{C}H_2OH + H_2O \quad (3)$$

$$C_6H_5N(CH_3)_2 + \overset{+}{C}H_2OH \xrightarrow{k_4} p\text{-}\overset{+}{C}H_2C_6H_4N(CH_3)_2 + H_2O \quad \text{(slow)} \quad (4)$$

$$(CH_3)_2NC_6H_5 + p\text{-}\overset{+}{C}H_2C_6H_4N(CH_3)_2 \longrightarrow p\text{-}(CH_3)_2NC_6H_4CH_2C_6H_4N(CH_3)_2\text{-}p' + H^+ \quad \text{(fast)} \quad (5)$$

The rate of consumption of FA is given by

$$dx/dt = k_4[C_6H_5N(CH_3)_2][\overset{+}{C}H_2OH] \quad (6)$$

where k_4 is the rate constant of step (4). The concentration of undissociated DMA and that of the conjugate acid of FA are calculated as follows

$$[C_6H_5N(CH_3)_2] = \frac{d - 2x}{1 + K_1a_{HCl} + K_1K_2\,(a_{HCl}/a_{Cl^-})}$$

$$[\overset{+}{C}H_2OH] = \frac{f - x}{1 + ([H_2O]/K_3a_{H_3O^+})}$$

where K_1, K_2 and K_3 are the equilibrium constants of equations (1), (2) and (3), and a_{HCl}, a_{Cl^-}, $a_{H_3O^+}$, the activities of HCl, Cl^- and H_3O^+, respectively. Then equation (6) is replaced by

$$\frac{dx}{dt} = \frac{k_4}{\left\{1 + K_1a_{HCl^+} + K_1K_2\,\frac{a_{HCl}}{a_{Cl^-}}\right\}\left\{1 + \frac{[H_2O]}{K_3a_{H_3O^+}}\right\}}(d - 2x)(f - x) = k(d - 2x)(f - x) \quad (7)$$

the integration of which leads to the equation already employed in the calculation of k. By utilizing the rate equation (7), the effects of the activities of oxonium and chloride ion and that of undissociated acid upon the rate constant k are considered below. Since the value of $[H_2O]/K_3a_{H_3O^+}$ is very large (K_3, 0.89×10^{-4} at 23.4°),[7] equation (7) reduces to

$$\frac{K_3K_4}{k[H_2O]} = \frac{1}{a_{H_3O^+}} + \frac{K_1a_{HCl}}{a_{H_3O^+}} + K_1K_2\,\frac{a_{HCl}}{a_{H_3O^+}a_{Cl^-}} \quad (8)$$

From experiments 3 and 8–11, when the acid is present equivalent to DMA, *p*H of the solution is nearly independent of their concentrations, *i. e.*, the equilibrium $HCl + H_2O \rightleftarrows H_3O^+ + Cl^-$ is hardly affected by the further addition of DMA hydrochloride. Consequently, $a_{H_3O^+}$ and $a_{HCl}/a_{H_3O^+}$ in equation (8) is nearly constant in a series of these experiments and if it is assumed that the activity coefficient of chloride ion is constant, the relation $\Delta(1/k)/\Delta(1/[Cl^-])$ = constant (Δ means the difference between two values and $[Cl^-]$ the concentration of chloride ion) will hold with acid catalysis as indicated in Table II.

TABLE II

THE RELATION BETWEEN RATE CONSTANT AND ANION CONCENTRATION WITH VARIOUS MOLAR RATIOS OF DIMETHYLANILINE TO FORMALDEHYDE

	$\Delta(1/k)$	$\Delta(1/[Cl^-])$	$\Delta(1/k)/\Delta(1/[Cl^-])$
	HCl–catalyzed		
No. 8:3	0.74×10^4	5.0	1.5×10^3
No. 9:3	$.22 \times 10^4$	1.7	1.3×10^3
No. 10:3	$-.12 \times 10^4$	−1.0	1.2×10^3
No. 11:3	$-.21 \times 10^4$	−1.7	1.2×10^3

	$\Delta(1/k)$	$\Delta(1/[SO_4^=])$	$\Delta(1/k)/\Delta(1/[SO_4^=])$
	H_2SO_4–catalyzed		
No. 17:14	0.27×10^4	10.0	2.7×10^2
No. 18:14	$.07 \times 10^4$	3.3	2.1×10^2
No. 19:04	$-.05 \times 10^4$	−2.0	2.5×10^2
No. 20:14	$-.08 \times 10^4$	−3.3	2.4×10^2

With respect to experiments 1–7, in which the oxonium-ion activities vary, accurate consideration is difficult, since no data are available as to a_{HCl} or K_1 and K_2 at 80°. At any rate, as the values of K_1 and K_2 will probably be much larger than 1, the third of three terms in equation (8) seems to have the greatest influence on the k value. With experiments 4–6, $a_{H_3O^+}$ varies but little with the addition of sodium chloride and may appear to have the same relation as in

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[7] Wadano, Trogus and Hess, *Ber.*, **67**, 174 (1934); calculated from $K_B = 1.62 \times 10^{-20}$.

nos. 8–11 mentioned above, but calculation showed that the values of $\Delta(1/k)/\Delta(1/[\mathrm{Cl}^-])$ varied and were lower than above. This is probably due to the fact that k increases more than predicted from equation (8) owing to the chloride ion catalysis as stated above. As to experiments 1–3 and 12–14, in which acid is present more than the equivalent of DMA, the activity coefficient of acid–anion and oxonium-ion will decrease with acid concentration while that of undissociated acid will increase and, consequently, the third term in equation (8) will increase. This deduction agrees with the experimental data, which show that the higher acid concentration corresponds to the lower reaction rate.

Summary

The hydrochloric- or sulfuric-acid-catalyzed condensation of dimethylaniline with formaldehyde into p,p'-tetramethyldiaminodiphenylmethane was kinetically studied by the estimation of the consumed amount of formaldehyde (sulfite method), and following was recognized. 1. Formation of p-dimethylaminobenzyl alcohol (or benzylcarbonium ion) is rate-determining. 2. The rate is proportional to the product of the concentration of dimethylaniline and formaldehyde present. 3. The reaction is very slow in the absence of acid, but the excess acid again reduces the rate. 4. The addition of inorganic salt (*e. g.*, sodium chloride) increases the rate. The probable mechanism was postulated and the rate equation derived from it provided a satisfactory explanation for the obtained data.

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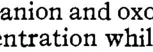
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Structure of Diketene and Butylketene Dimer

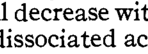
BY CHARLES D. HURD AND CATHERINE ANNE BLANCHARD

In 1936 Hurd and Williams proposed[1] as the structure for diketene an equilibrium mixture of 2-butenoic β-lactone (I) and acetylketene, CH_3-CO—CH=C=O, the most critical evidence in its



$$\begin{array}{lll} CH_3{=}C & {=} & CH \\ \quad\ \ | & & | \\ \quad\ \ O & — & CO \end{array}$$

I



$$\begin{array}{lll} CH_2{=}C & — & CH_2 \\ \quad\ \ | & & | \\ \quad\ \ O & — & CO \end{array}$$

II

favor being the formation of a phenylhydrazine derivative of m. p. 144–145° from the products of ozonolysis of diketene. This was interpreted as representing pyruvaldehyde bisphenylhydrazone. Values reported in the literature[2] for this compound are 145, 147–148, 148, 154°.

A. L. Wilson proposed[3] for diketene structure II, or 3-butenoic β-lactone. On ozonolysis, a compound of this structure should yield formaldehyde and malonic acid. Since formaldehyde phenylhydrazone[4] melts at 145°, it is apparent that this could have been the phenylhydrazine derivative obtained by Hurd and Williams.

Recent work[5] from various approaches has produced new evidence which is more readily explained by II than I, hence the ozonolysis of diketene has been reinvestigated. If formaldehyde and malonic acid were both characterized and if pyruvaldehyde was absent, this would become additional evidence in favor of II. Such, indeed, proved to be the findings.

To gain experience, styrene and benzylideneacetone were ozonized and the ozonide hydrolyzed in the presence of zinc dust. Formaldehyde was formed in 57% yield (as the methone derivative) from the former and pyruvaldehyde in 37% yield (as the bisphenylhydrazone) from the latter. These yields of aldehydes are of the same order as those obtained by Church, Whitmore and McGrew[6] when hydrolyzing various ozonides under like conditions: formaldehyde, 6–35%; acetaldehyde, 38%; butyraldehyde, 27%; valeraldehyde, 38%.

Since malonic acid as such was not found in the earlier work,[1] attention was directed to more delicate methods of characterization. It was found that small quantities of this acid could be identified as cinnamylidenemalonic acid.

Purified diketene was then subjected to ozonolysis. Formaldehyde was characterized not only as the methone derivative in 30% yield but also as the 2,4-dinitrophenylhydrazone. No evidence for pyruvaldehyde could be found. Malonic acid, as cinnamylidenemalonic acid, was established as a product of the ozonolysis. This evidence, therefore, supports 3-butenoic β-lactone as the structure of diketene.

It should be pointed out that the above evidence does not prove that diketene is homogeneously represented by structure II. Any acetylketene present, however, must be trivial since its quantity must be too small to give rise to recognizable quantities of pyruvaldehyde on ozonolysis. 2-Bu-

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(1) Hurd and Williams, This Journal, **58**, 962 (1936).

(2) von Pechmann, *Ber.*, **20**, 2453 (1887); Dieckmann and Platz, *ibid.*, **38**, 2990 (1905); Pinkus, *ibid.*, **31**, 36 (1898); Nef, *Ann.*, **335**, 255 (1904).

(3) See Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

(4) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 2nd ed., 1940 p. 188.

(5) Taufen and Murray, This Journal, **67**, 754 (1945); Whiffen and Thompson, *J. Chem. Soc.*, 1005 (1946); Wassermann, *ibid.*, 1323 (1948); Blomquist and Baldwin, This Journal, **70**, 29 (1948); Miller and Koch, *ibid.*, **70**, 1890 (1948).

(6) Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).