Equation VI may also be derived by assuming that the radicals are contained in a cylinder with a Gaussian distribution around the axis of the cylinder.[7] Otherwise the assumptions are essentially the same and the factors in the final equation have the same physical significance.

The total production of hydroxyl radicals in the ceric–formic acid system and hence the total radical pair yield expressed in micromoles is twice the amount of oxygen produced plus one-half the increase in the production of cerous ion caused by the addition of the formic acid. The numerical value is 2 × 42 plus one-half 310 for a total of 239. A corresponding calculation can be made for the oxidation of ferrous solutions by dissolved oxygen using the same radiation. In that case, if we accept Hart's[8] mechanism, the total amount of ferrous ion oxidized (ferric ion formed) is given by the number of hydroxyls reacting with the ferrous ion plus twice the number of moles of peroxide formed by the reaction we have listed as 2a, plus three times the number of HO_2 radicals (formed by the reaction 3 in our mechanism). If we combine this statement with the fact that the total numbers of hydrogen atoms and hydroxyl radicals formed must be equal we find that the total number of radical pairs produced is one-fourth the sum of the number of moles of ferric ion and six times the amount of hydrogen formed. In a ten-hour irradiation of such a ferrous solution in our reaction cell we found that the amount of ferric produced was 719 micromoles and the hydrogen was 35.3. These values lead to a radical yield of 233, which we consider to be in excellent agreement with the one obtained for the ceric–formic system. This agreement may be taken as lending support to both mechanisms and to the idea that under the limiting conditions all of the radicals produced are entering into secondary reactions.

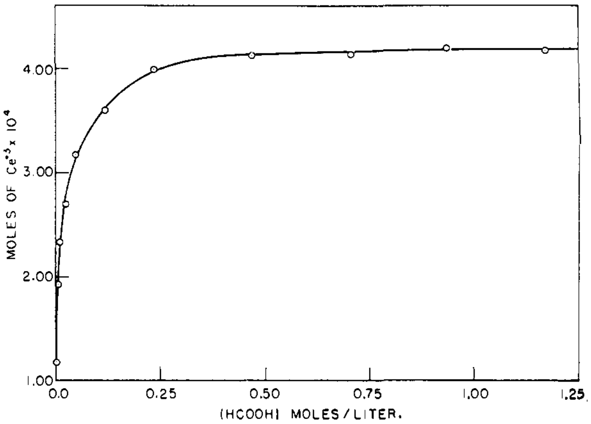

Fig. 3.—Cerous ion produced as a function of the formic acid concentration.

BERKELEY, CALIFORNIA

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(8) E. J. Hart, THIS JOURNAL, **73**, 1891 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SIR JOHN CASS COLLEGE]

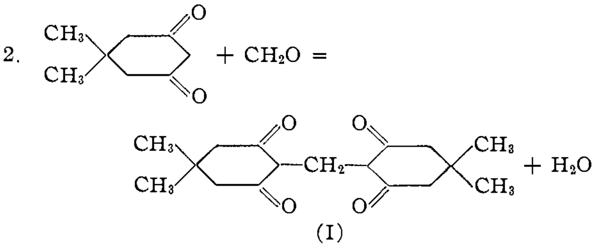
The Kinetics and Mechanism of the Reaction of Formaldehyde with Dimedone. Part I

BY D. SPENCER AND T. HENSHALL

RECEIVED JULY 2, 1954

A kinetic study has been made of the reaction between dimedone and formaldehyde under both acid and alkaline conditions. The reaction has been shown to be of the first order with respect to both reactants. The reaction rate is considerably affected by the hydrogen-ion concentration of the solution, and reaches a maximum value at *p*H 8.5. A reaction sequence based on an ion-polar molecule interaction has been proposed. From this, on analysis, a rate equation has been derived which is in close agreement with the experimental results over the *p*H range of 1 to 14.

The reaction between dimedone (5,5-dimethylcyclohexanedione-1,3) and formaldehyde is represented stoichiometrically as a simple condensation of one molecule of formaldehyde with two molecules of dimedone by the elimination of one molecule of water according to



(I)

The nature of possible intermediates in this reaction is suggested[1] by the closely related, though often considerably more complex condensation products of formaldehyde with phenols in which, under certain conditions, almost quantitative yields of methylene compounds similar in structure to I can be obtained.

Moreover, a quantitative analytical study of the reaction of dimedone and formaldehyde,[2] in which the amounts of I precipitated in a given time from buffer solutions containing known amounts of the aldehyde with a slight excess of dimedone were determined, showed (a) that a theoretical yield of product was obtained only at *p*H 4.6 and (b) that in solutions more acid than this, the yield of product diminished rapidly, even on allowing the reaction mixture to stand for many days.

The lower yield of I obtained above *p*H 4.6 may be reasonably interpreted as a solubility effect; but the decrease in yield in more acid solutions could not be accounted for unless it be assumed that the rate of formation of I decreased rapidly with in-

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(1) J. F. Walker, "Formaldehyde," Reinhold Publ. Corp., New York, N. Y., 1944.

(2) J. H. Yoe and L. C. Reid, *Ind. Eng. Chem., Anal. Ed.*, **13**, 238 (1941).

crease of the hydrogen ion concentration of the solution. This implies further, that the reactive form of dimedone is the dimedone ion (D^-) and that the reaction is of the ion-polar molecule type. Evidence is here presented in favor of such a proposal.

Experimental

Materials.—Dimedone (reagent grade, L. Light and Co.) was recrystallized from aqueous alcohol, needles m.p. 147°.

Formaldehyde Solution.—This was prepared by dilution of a 40% solution, and standardized by the hydroxylamine method.[3]

Compound I.—1,3,1',3'-Tetraketo-5,5,5',5'-tetramethyl-4,4'-dicyclohexylmethane) was prepared for identification purposes by adding formaldehyde solutions (20 ml. of 40% solution) to a solution of dimedone (5 g.) in hot ethanol (30 ml.) and water (5 ml.). The white precipitate which separated was filtered, and recrystallized from aqueous ethanol; m.p. 191°.

Determination of the Order of Reaction

(a) **With Respect to Dimedone, *i.e.*, with Formaldehyde in Excess.**—The procedure to be described is based on the observation that the reaction of dimedone and formaldehyde is effectively stopped in strongly acid solution; complete precipitation of the condensation product, compound I, is thus assured, and filtration can be carried out at leisure.

A weighed quantity of dimedone was dissolved in ethanol (3 ml.) and then diluted with buffer solution to a standard volume of 200 ml. This solution, in a conical flask, was immersed in a thermostat at 25 ± 0.02°. The formaldehyde solution (1 ml. 40%) was added, and after a fixed interval, the reaction was stopped by the addition of concentrated hydrochloric acid (25 ml.). After standing for 15 minutes, the precipitate was filtered through a weighed sintered glass filter. The precipitate, after washing thoroughly with distilled water, was dried at 100° for 0.75 hr. and then weighed. Measurements were carried out in two buffer solutions; one, *M*/20 potassium hydrogen phthalate solution, at *p*H 4.00; and the other, a citric acid–sodium phosphate solution[4] at *p*H 3.03. The results are given, respectively, in Tables I and II, which indicate that the reaction is first order with respect to dimedone.

Table I

M/20 potassium hydrogen phthalate, *p*H 4.00.

Time of reaction t, sec.	Wt. of product, g.	Initial concn., dimedone C_0, mole/l.	Concn. of dimedone at time, t, (C)	$\frac{\log_{10} C_0/C}{t} \times 10^2$
60	0.0323	0.00600	0.00489	0.15
120	.0602	.00584	.00379	.16
180	.0871	.00584	.00318	.15
240	.1004	.00600	.00258	.15
300	.1186	.00592	.00187	.17
600	.1576	.00599	.00611	.17
			Mean	.16

Table II

Citric acid/sodium phosphate solution, *p*H 3.03.

Time of reaction t, sec.	Wt. of product, g.	Initial concn., dimedone (C_0), mole/l.	Concn. after t, sec. (C)	$\frac{\log_{10} C_0/C}{t} \times 10^3$
420	0.0427	0.00583	0.00438	0.30
540	.0484	.00600	.00434	.26
810	.0709	.00596	.00351	.28
1200	.0940	.00597	.00277	.28
1380	.1050	.00600	.00241	.29
1440	.1058	.00592	.00230	.29
1443	.1085	.00576	.00219	.29
1590	.1142	.00583	.00184	.30
1710	.1224	.00577	.00159	.33
1800	.1281	.00598	.00162	.32
2520	.1500	.00590	.000782	.35
2250	.1393	.00573	.00098	.34
			Mean	.30

(b) **With Respect to Formaldehyde, i.e., with Dimedone in Excess.**—A slightly different procedure was used here, in that the dimedone (1.5 g.) was dissolved in glacial acetic acid (20 ml.) and diluted with water to 200 ml. To this solution, after standing in a thermostat at 21° (±0.02°), formaldehyde solution (3 ml., 0.00508 g./ml.) was added, and the whole vigorously stirred. The reaction was timed from this addition to the moment of filtration through a sintered glass filter. The product was washed and dried for 40 min. at 100°. The results are given in Table III.

Table III

Time of reaction t, sec.	Wt. of product, g.	$\frac{\log_{10} C_0/C}{t} \times 10^5$
0	....	..
3,600	0.0197	1.76
3,400	.0260	1.55
7,200	.0400	1.90
10,340	.0542	1.92
12,600	.0610	1.83
14,580	.0698	1.90
19,080	.0816	1.82
21,600	.0910	1.92
25,200	.0994	1.91
29,400	.1055	1.85
32,400	.1131	1.92
36,600	.1185	1.91
39,840	.1208	1.89
42,780	.1258	1.90
	Mean	1.89

The Over-all Order of Reaction.—The over-all order of reaction was determined from rate measurements on buffered solutions containing equivalent proportions of formaldehyde and dimedone, that is, in which the concentration of dimedone is twice that of formaldehyde.

Procedure.—Sodium acetate (2 g.) was added to a solution of dimedone (0.142 g.) in glacial acetic acid (8 g.), and the whole diluted to 200 ml. with distilled water. This buffered dimedone solution was allowed to attain a steady temperature, and then formaldehyde solution (3 ml., 0.00508 g./ml.) added. The reaction mixtures were removed after various reaction times and the reaction product estimated in the manner described earlier. The results are given in Table IV, which shows clearly that the reaction is over-all of the second order.

Table IV

Time of reaction t, sec.	Wt. of product, g.	$\frac{(1/C - 1/C_0)}{t} \times 10^2$
1230	0.0364	1.06
2145	.0525	1.02
3270	.0695	1.09
4170	.0802	1.12
4990	.0865	1.12
	Mean	1.08

However, since in this reaction dimedone is consumed twice as fast as formaldehyde, the integrated form of the second-order rate equation for this case is

$$k = \frac{2.303}{t(a/2 - b)} \times \log_{10} \frac{2b}{a} \times \frac{(a/2 - x)}{(b - x)}$$

in which "*a*" and "*b*" are the initial concentrations of dimedone and formaldehyde, respectively. For the particular case in which $a = 2b$, which is considered above

$$k = \frac{1}{2t}\left[\frac{1}{(b - x)} - \frac{1}{b}\right] = \frac{1}{2t}\left[\frac{1}{c} - \frac{1}{c_0}\right]$$

Hence the second-order rate constant at 21° is 0.54×10^{-2}.

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[3] W. M. D. Bryant and D. M. Smith, This Journal, **57**, 57 (1935).

[4] H. T. S. Britton, "Hydrogen-ions," Chapman and Hall, London 1929, p. 182.

Effect of *p*H on the Second-order Rate Constant.—Measurements of the rate of reaction were carried out at constant temperature in buffered solutions covering the *p*H range 1.2 to 12.4.

For the *p*H range 3.2 to 7.0 the buffer solutions were prepared by mixing solutions of $M/5$ Na_2HPO_4 and $M/10$ citric acid,[4] while for the *p*H range 7 to 12.4, mixtures of sodium borate and hydrochloric acid or sodium hydroxide were used.[5]

The *p*H values of the buffer solutions were checked on the glass electrode assembly.

The results of these measurements are set out in Table V.

TABLE V

*p*H	$k \times 10^2$	*p*H	$k \times 10^2$
1.2	0.0019	7.0	92
3.2	1.35	8.6	92
3.4	2.15	9.2	88
3.6	3.2	10.0	78
4.0	6.8	11.1	69
4.2	9.7	12.4	53
4.4	14.6	13.0	41
5.0	40.7	13.5	30
6.0	77	13.7	15[a]

[a] Value extrapolated to zero time.

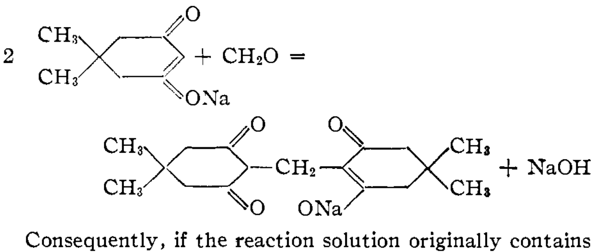
A potentiometric titration of a dilute aqueous alcoholic solution of dimedone, the concentration of which was of the same order as that used in the rate measurements indicated that dimedone is completely ionized at *p*H 8.5, while from Table V, the maximum rate is seen to occur in the neighborhood of *p*H 8.

This correlation between the rate of reaction and the proportion of ionized dimedone present was further demonstrated by direct measurements of the variation in reaction rate with the molar proportion of sodium hydroxide. The results of such measurements are given in Table VI and plotted in Fig. 1.

TABLE VI

Mole ratio $\frac{\text{alkali}}{\text{dimedone}}$	Rate constant at 25° $k \times 10^2$	Mole ratio $\frac{\text{alkali}}{\text{dimedone}}$	Rate constant at 25° $k \times 10^2$
..	3.10	0.80	44.8
0.16	14.1	1.0	62
0.32	28.6	1.04	65
0.48	39.5	1.12	58
0.54	34.5	1.2	57
0.58	35.7	1.28	58
0.64	37.4	1.60	58
0.72	41.8		

The irregularities in Fig. 1 are due mainly to the uncertainties in the rate constants obtained in these experiments for the rate of reaction was found to increase as the reaction proceeded. The reason for this change in rate is due to change in dimedone ion concentration resulting from the liberation of alkali as reaction proceeds according to



Consequently, if the reaction solution originally contains free dimedone, then as reaction proceeds this will be ionized by the alkali liberated, the increase in (D^-) will thus be shown by an increased reaction rate. This effect is indicated in Table VII.

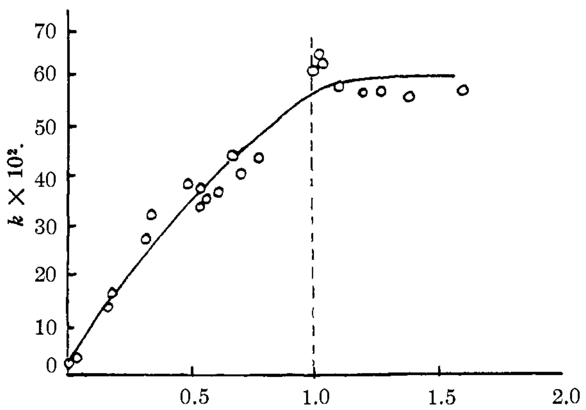


Fig. 1.

The "Ionization" Salt Effect. Procedure.—Dimedone (0.1682 g.) was dissolved in ethyl alcohol (3 ml.) a known weight of sodium chloride added, and the mixture dissolved in water to a total value of 200 ml. After attaining a steady temperature, formaldehyde solution (3 ml., 0.004903 g./ml.) was added and the product obtained after various reaction times determined gravimetrically as before. The results are set out in Table VIII.

TABLE VII

Temperature 25°, mole ratio alkali/dimedone = 0.5.

Reaction time, sec.	$1/c$, l./mole	$k \times 10^2$
0	351	..
120	427	31.7
240	518	34.8
360	682	46
620	975	50
1320	1950	61

TABLE VIII

Wt. of salt, g.	Ionic strength, μ	$\sqrt{\mu}$	$k \times 10^2$ (at 25°)
....	...	..	3.10
0.130	0.019	0.14	3.39
0.462	.039	.20	3.55
0.506	.043	.21	3.80
1.134	.096	.31	3.80
1.506	.130	.36	3.96
2.022	.170	.41	4.00
4.812	.400	.63	4.23
5.029	.420	.65	4.23
8.106	.690	.83	4.28
12.501	1.10	1.05	4.18
18.157	1.50	1.2	4.20
22.038	1.90	1.4	4.22
26.614	2.70	1.6	4.03

The increased ionization of dimedone resulting from the addition of a strong electrolyte was determined approximately by measuring the change produced in the *p*H of a half-neutralized solution of dimedone and applying the approximate form of the Henderson equation

$$pH = pK_a + \log_{10} \frac{(\text{salt})}{(\text{acid})}$$

The results obtained are given in Table IX and plotted in Fig. 4.

(b) **Primary Kinetic Salt Effect.**—The small variation with *p*H in reaction rate over the *p*H range 8 to 9.2 (Fig. 2), facilitated a study of the effect of salt concentration on the reaction rate in this region as a means of estimating the magnitude of the primary kinetic salt effect. The reaction was carried out in $M/20$ sodium borate solution and the ionic strength varied as before. The results are given in Table X.

The Energy of Activation.—The energy of activation for this reaction was obtained from the temperature variation

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[5] W. G. Palmer, "Practical Physical Chemistry," Cambridge Press, 1949, p. 234.

TABLE IX

Wt. of potass. chloride, g.	Ionic strength μ	$\sqrt{\mu}$	pH at 25°	pK_o	$\log_{10} K_c$	K_c, × 10^7
0.00	..	..	5.170	5.166	$\bar{6}.834$	68
1.45	0.1	0.31	5.103	5.099	$\bar{6}.901$	80
7.25	0.5	0.70	5.078	5.074	$\bar{6}.926$	84
14.5	1.0	1.0	5.070	5.066	$\bar{6}.934$	86
21.70	1.5	1.2	5.109	5.105	$\bar{6}.895$	79
29.0	2.0	1.4	5.137	5.133	$\bar{6}.867$	74
33.5	3.0	1.7	5.159	5.155	$\bar{6}.845$	70

TABLE X

The *p*H of a *M*/20 solution of sodium borate changes by only 0.7 of a *p*H unit over this range of ionic strength.

Ionic strength, μ	$k \times 10^2$ (at 25°)
0.17	89
0.34	98
0.84	105
1.64	114

of the second-order rate constant over a temperature range of 20° and in *M*/20 potassium phthalate buffer solution, the temperature coefficient of which is known to be small.

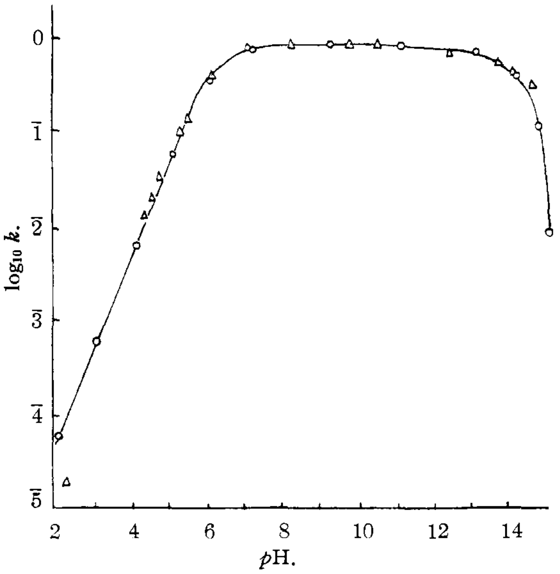


Fig. 2.—○, theory; △, expt.

The determinations were carried out by mixing dimedone and formaldehyde in equivalent amount in *M*/20 phthalate buffer solution and precipitating the product after fixed time intervals by the addition of excess concentrated hydrochloric acid as previously described.

The results of these experiments are given in Table XI. The values of energy of activation given in the last column of the table were calculated from the Arrhenius equation in the form

$$\log_{10} \frac{k_T/k_{298}}{\frac{1}{298} - \frac{1}{T}} = \frac{E_a}{2.303R}$$

The value obtained was 16.4 kcal.

TABLE XI

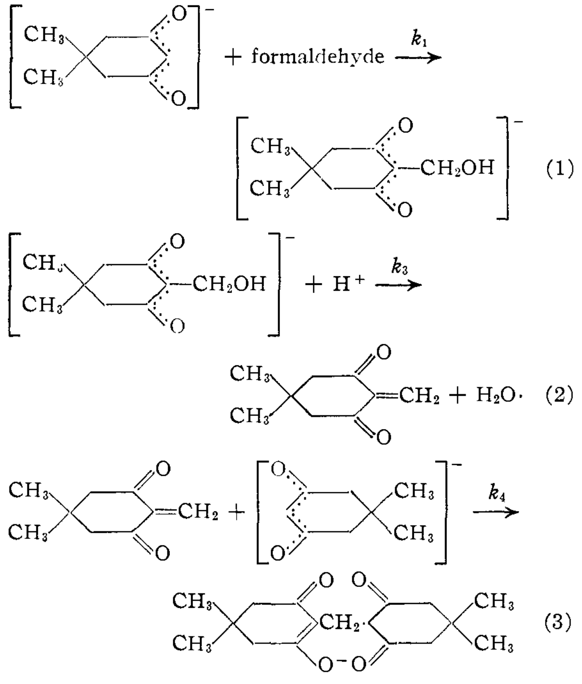
Temp., °C.	$1/T$, °K. × 10^2	Rate $k \times 10^2$	$E_a/2.303R$, cal./mole
25.0	0.3356	6.0, 6.3	
30.2	.3298	9.9, 9.8	3530
36.4	.3231	18.1, 18.1	3780
39.3	.3202	21.6, 22.1	3570
45.3	.3142	34.6, 36.0	3530
		Mean	3600

Discussion

The reaction between dimedone and formaldehyde has been shown to be over-all of the second order (Tables I to IV), and to be considerably affected by the hydrogen ion concentration of the solution (Table V).

In strongly acid solutions, dimedone may be considered to exist in the non-ionized enolic form, and since the rate of reaction is extremely small under these conditions, it may be assumed that this form of the dimedone molecule is unreactive toward formaldehyde.

Since the reactive form of dimedone appears to be D^-, the following reaction sequence is proposed



Now formaldehyde is known to exist in concentrated solutions in the form of an equilibrium mixture of the monohydrate $CH_2(OH)_2$, and low molecular weight polyoxymethylene compounds, $HO(CH_2O)_nH$; but in the dilute solutions used in this investigation, the formaldehyde is considered to exist essentially as the monohydrate.[1]

Further, the rate of dehydration of aldehyde hydrates in aqueous solution does not appear to be a step controlling their rates of reaction, and Bell[6] has shown that the rate of dehydration of acetaldehyde hydrate is much greater than the self condensation to aldol. Accordingly, the reaction sequence above may be augmented by the further fast stage

$$CH_2(OH)_2 \longrightarrow CH_2O + H_2O$$

so that the nature of the formaldehyde in stage (1) is specified.

If now stage (1) is rate determining, then the over-all rate of reaction may be expressed by equation 4

$$v = k_1(D^-)(CH_2O) \qquad (4)$$

The rate constants given in Tables IV and V were

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(6) R. P. Bell, *Trans. Faraday Soc.*, **37**, 716 (1941).

calculated on the basis of equations 5 in which $(D)_T$ is the total dimedone concentration.

$$v = k(D)_T(CH_2O) \qquad (5)$$

From (4) and (5)

$$k = \frac{(D^-)}{(D^-) + (D)} k_1 = \frac{k_1}{(H^+)/K_a + 1} \qquad (6)$$

Hence values of k at various hydrogen ion concentration may be calculated from equation 6, assuming that $k_1 = 0.92$ at pH 8.5 (Table V), and $K_a = 0.68 \times 10^{-5}$; the values of k so calculated are given in Table XII.

TABLE XII

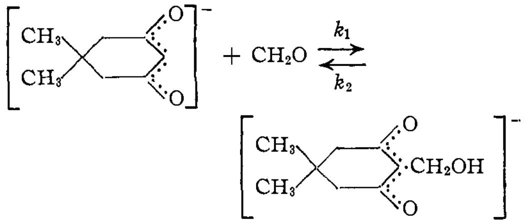
pH	(H^+)	k calcd.
8.0	10^{-8}	0.92
7.0	10^{-7}	.91
6.0	10^{-6}	.80
5.0	10^{-5}	.37
4.0	10^{-4}	.059
3.0	10^{-3}	.0061
2.0	10^{-2}	.00061
1.0	10^{-1}	.000061

The close agreement between these and the experimental k values may be seen in Fig. 2.

Equation 6, for reaction in feebly acid solutions, predicts that the reaction rate will increase to pH 8.5, and then will remain constant for more alkaline solutions.

However, the rate of reaction decreases rapidly in strongly alkaline solution even though dimedone is completely ionized under these conditions.

If now we replace equation 1 by the reversible stage (7), then the rate of reaction is now given by (8), or the rate constant by (9)


(7)

$$v = k_1(CH_2O)(D^-) - k_2(DCH_2OH^-) \qquad (8)$$

$$k = k_1 - \frac{k_2(D \cdot CH_2OH^-)}{(CH_2O)(D^-)} \qquad (9)$$

Application of the stationary state condition to the concentration of the intermediate DCH_2OH^-, gives (10), and combination of (9) and (10) gives (11)

$$(DCH_2OH^-) = \frac{k_1(D^-)(CH_2O)}{k_2 + k_3(H^+)} \qquad (10)$$

$$k = k_1 - \frac{k_1}{1 + \frac{k_3}{k_2}(H^+)} \qquad (11)$$

The value of the ratio k_3/k_2 can be obtained from (11) by substitution of experimental data. Thus from Table V, at pH 13.7, $(H^+) = 2 \times 10^{-14}$, $k = 0.15$ and $k_1 = 0.92$, so that k_3/k_2 has the value 0.97×10^{13}. Equation 11 thus gives the relationship between the rate constants calculated from (5) and the hydrogen ion concentration of the solution. Values of k calculated from (11) are compared with experimental values in Table XIII.

TABLE XIII

(H^+)	k Calcd.	k Obsd.	(H^+)	k Calcd.	k Obsd.
1×10^{-14}	0.01	..	10^{-12}	0.81	0.57
2×10^{-14}	.15	(0.15)	10^{-11}	.91	.70
3.3×10^{-14}	.22	.30	10^{-10}	.92	.78
10^{-13}	.45	.41	10^{-9}	.92	.88
			10^{-8}	.92	.92

Although equation 11 does predict correctly that the rate will decrease in alkaline solution, there are slight deviations from the experimental results. Such deviations are, however, to be expected since the reaction scheme postulated may possibly be over-simplified. Nevertheless the agreement between the theoretical and the experimental results (Fig. 2) is striking and is considered sufficient to justify the assumptions that have been made.

Finally, the theoretical rate equation for the reaction in aqueous solutions of varying hydrogen-ion concentration over the whole pH range, and derived on the basis of the mechanism proposed above is

$$k = \frac{k_1}{(H^+)/K_a + 1} - \frac{k_1}{1 + 0.97 \times 10^{13}(H^+)} \qquad (12)$$

The agreement between this equation and the experimental results in both acid and alkaline solutions is shown in Fig. 2.

The order of magnitude of the constant, $k_3/k_2 = 10^{13}$, is interesting since it is in agreement with the consideration of stage (2) in the reaction mechanism as a relatively fast step.

The Effect of Neutral Salts.—If the reaction is of the ion-polar molecule type, then it would be expected that the addition of neutral salts would influence the rate of reaction through the operation of the primary kinetic salt effect. Such an effect has been observed, and is indicated in Table X.

There is, however, yet another way in which the addition of a neutral salt can influence the rate of a reaction such as that between dimedone and formaldehyde: this involves an increase in the ionization of dimedone in the presence of added electrolyte, and may be termed an "ionization salt effect."

The determinations of reaction rate in the presence of increasing amounts of added electrolyte are summarized in Table VIII, and expressed diagrammatically in Fig. 3. For comparison, values of K_c, the concentration dissociation constant of dimedone, determined at various ionic strengths of solu-

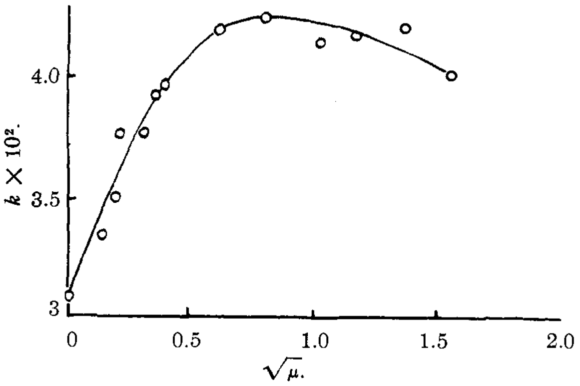


Fig. 3.

tion are shown in Fig. 4. It will be noted that both curves pass through a maximum in the neighborhood of unit ionic strength.

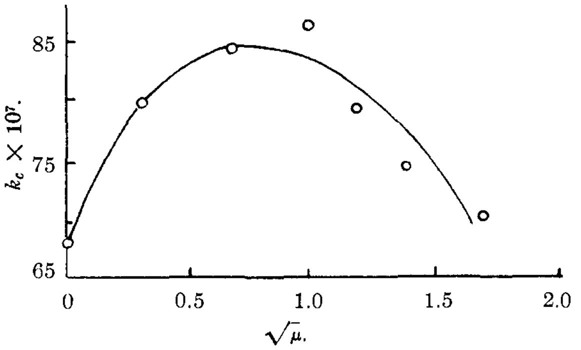


Fig. 4.

Since in unbuffered aqueous solutions of dimedone both (H^+) and (D^-) are small compared with (D) so that $(D^-)^2$ is proportional to K_c, then the percentage increase in the concentration of ionized dimedone produced by an increase in K_c is given by (13).

$$\frac{(D^-)_2 - (D^-)_1}{(D^-)_1} \times 100 = \frac{\sqrt{K_{c(2)}} - \sqrt{K_{c(1)}}}{\sqrt{K_{c(1)}}} \times 100 \quad (13)$$

In Table VIII, the values of K_c increase from 6.8×10^{-6} to 8.6×10^{-6} and the ionic strength of solution is increased from zero to unity, so that (D^-) increases by some 12.5%. The increase in rate due to this cause, together with that due to the primary kinetic salt effect, accounts mainly for the total observed kinetic salt effect which was of the order of a 40% increase in reaction rate as the ionic strength is raised from zero to unity. The effects are shown qualitatively in Fig. 5.

The Frequency Factor.—The Arrhenius activation energy, determined in the usual way, was found to be 16.4 kcal. This leads to a value of the frequency factor of 10×10^{11} at 25°, which is rather close to the average value of 2.77×10^{11} for collision frequencies in solution,[7] and it has been previously pointed out that such agreement is characteristic of the reactions of ions with polar molecules.[8]

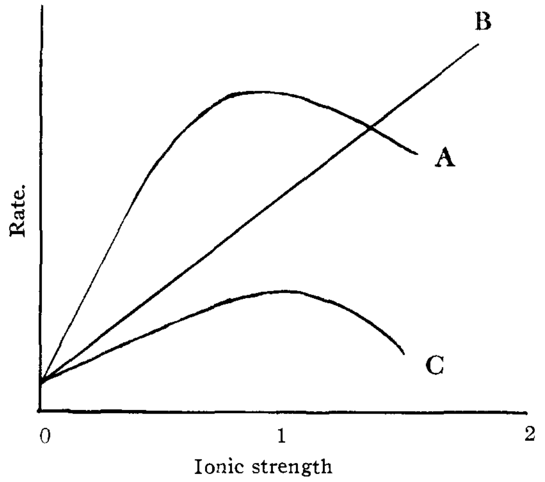


Fig. 5.—A, total salt effect; B, primary kinetic salt effect; C, "ionization" salt effect.

Conclusion.—Finally it may be said that this kinetic study has shown that the reaction between dimedone and formaldehyde is considerably more complex than has previously been supposed. The mechanism which has been postulated for the reaction has been shown to provide a reasonable interpretation for the kinetics under both acid and alkaline conditions and the rate equation derived from this mechanism agrees closely with the experimental data.

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(7) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, New York, N. Y., 1947, p. 70.

(8) Ref. 7, p. 72.