429. *Quantitative Aspects of the Base-catalysed Reaction of Aliphatic Aldehydes with Iodine. Part I. Formaldehyde.*

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In strongly alkaline solution, iodine oxidises formaldehyde quantitatively to formic acid. The reaction is of the first order with respect to both iodine and aldehyde, but the dependence of rate on pH is more complex. Under the experimental conditions used, the active oxidising agents are hypoiodous acid and the hypoiodite ion, and formaldehyde exists predominantly as methanediol and the corresponding hydroxymethoxyl ion. Analysis of the kinetic relations indicates that binary interaction occurs between all possible pairs of the reactive species and enables the relative contributions of the various constituent reactions to be assessed. The hydroxymethoxyl ion reacts faster than methanediol, but hypoiodous acid is more reactive than the hypoiodite ion.

STUDIES have already been reported [1] of the kinetics and stoicheiometry of the halogenation, in alkaline solution, of a number of aliphatic ketones. The present series of papers will describe similar investigations of the reactions of certain aliphatic aldehydes with iodine; we here deal with formaldehyde, which differs from its higher homologues in undergoing quantitative oxidation to formic acid over a wide range of pH.[2,3]

EXPERIMENTAL

Materials.—" AnalaR " formalin containing *ca.* 36% w/v of formaldehyde was diluted with water to give an approximately 0·1M-solution. This was standardised by the sodium sulphite method [4] and then further accurately diluted as necessary, the concentrations of the resulting solutions being checked iodometrically.[2]

Kinetic Measurements.—Rate measurements were generally made in Y-tubes, since even at 0° the reactions are relatively rapid. The iodine and formaldehyde solutions were placed in one limb and an alkaline solution of the same total volume as the combined iodine and aldehyde solutions was run into the other. Control experiments confirmed that even after a long time no detectable oxidation of formaldehyde by iodine occurred in neutral solution. The reaction was started by tilting the Y-tubes to mix the reactants and was stopped after

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[1] Morgan, Bardwell, and Cullis, *J.*, 1950, 3190; Cullis and Hashmi, *J.*, 1956, 2512; 1957, 1548, 3080.

[2] Romijn, *Z. analyt. Chem.*, 1897, **36**, 18.

[3] Hatcher and Mueller, *Trans. Roy. Soc. Canada*, 1929, **23**, 35.

[4] Reynolds and Irwin, *Chem. and Ind.*, 1948, 419.

measured times by rapidly pouring the contents into a slight excess of hydrochloric acid and rinsing the tubes with a further small quantity of acid. The liberated iodine was immediately titrated with thiosulphate. Rates were calculated from the initial slopes of the iodine-concentration–times curves.

Preparation of Buffer Solutions and Measurement of pH.—The initial pH values of reaction mixtures ranged from 10 to 14 and an accurate knowledge of these was required. Since in kinetic runs the volume of alkaline solution added was always equal to that of the combined iodine and aldehyde solutions, a series of buffer solutions was prepared in which the required pH was obtained by dilution to twice the required volume. For the pH range 10—10·9, these contained various proportions of sodium carbonate and hydrochloric acid, for the range 11—12·4 mixtures of disodium hydrogen phosphate and sodium hydroxide, and for higher values solutions of sodium hydroxide alone. If the less alkaline buffer solutions are diluted with >0·005M-iodine solutions (instead of with water), the pH falls slightly. At this 0·005M concentration, however, which is that most frequently used in this work, no correction is necessary.

The pH of the diluted buffer solutions was measured with an " Alki " glass electrode and a pH meter.

RESULTS

General Kinetic Features.—Some typical plots of iodine consumption against time are shown in Fig. 1, which show that at 25° reaction is complete in about 5 min. and that exactly one mole of iodine is consumed per mole of formaldehyde initially present. Although it is known that under alkaline conditions formaldehyde is oxidised quantitatively to formic acid by an excess of iodine,[2,3] the results in Fig. 1 show that uptake of iodine is quantitative when its initial concentration is not in excess of the stoicheiometric value required by the equation: $CH_2O + I_2 + 3NaOH = H{\cdot}CO_2Na + 2I^- + 2Na^+ + 2H_2O$. Under the conditions used there is thus evidently no " wastage " of iodine as a result of disproportionation of hypoiodite to iodate: $3HIO \longrightarrow HIO_3 + 2HI$. However, if the iodine and alkali are mixed before addition of the formaldehyde, there is time for considerable disproportionation, and iodine uptake is no longer quantitative.

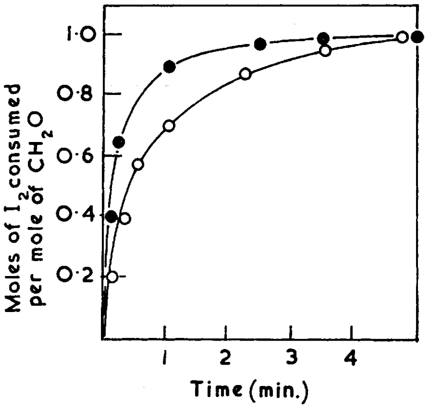

FIG. 1. The rate of consumption of iodine by formaldehyde.

Temp. = 25°; pH = 13·95.

○ [Iodine] = [Formaldehyde] = 0·0068M.

● [Iodine] = [Formaldehyde] = 0·02M.

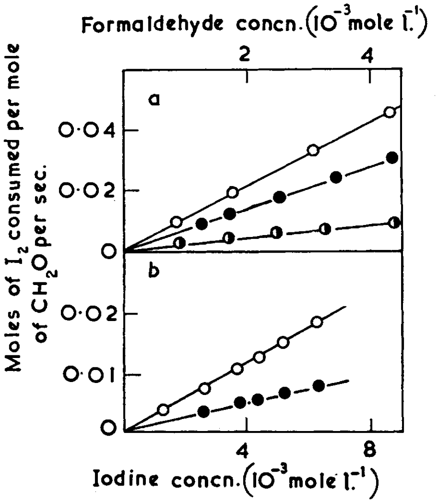

FIG. 2. The influence of formaldehyde and iodine concentration on the rate of iodine consumption at 0°.

a: [Iodine] = 0·0051M; pH, ○ = 13·9, ● = 13·22, ◑ = 12·0.

b: [Formaldehyde] = 0·0025M; pH, ○ = 13·22, ● = 12·0.

Influence of Formaldehyde and Iodine Concentrations.—Measurements of initial rates of iodine consumption at a given pH show that the reaction is of the first order with respect to formaldehyde (Fig. 2a). A similar result is found for the dependence of rate on iodine concentration (Fig. 2b); this contrasts with the behaviour of ketones [5] whose reaction is always of zero order with respect to the halogen. Each point in Figs. 2a and 2b represents the mean of at least three determinations of initial rate.

Influence of pH.—Fig. 3 shows the variation with pH of the initial rate of iodine consumption, which was investigated at several temperatures. Each point shown represents the mean value of at least three rate measurements. It is clear that an increase in pH accelerates the reaction although the observed relation is not simple. At each temperature studied, the curve tends to flatten in an intermediate region of pH but the rate increases again fairly sharply at higher pH values. Conversion of formaldehyde into formic acid is quantitative except at low pH values; under these conditions, the reaction is slow and hence, presumably, disproportionation of hypoiodite to iodate is sufficient to reduce very considerably the amount of iodine available in a suitably reactive form.

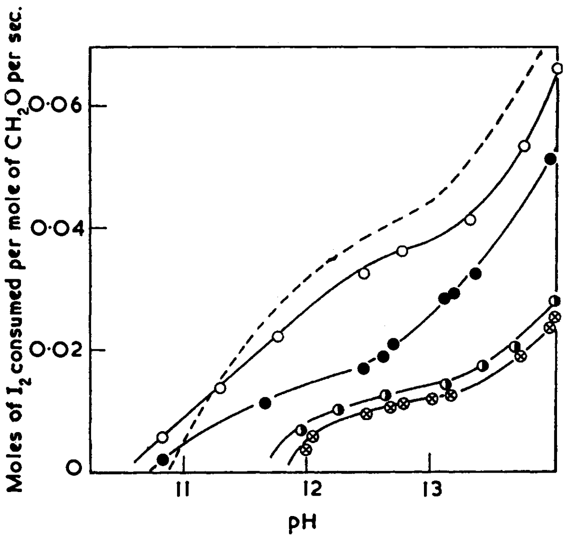

FIG. 3. The influence of pH on the rate of iodine consumption.

[Formaldehyde] = 0·0025M; [Iodine] = 0·0051M.

—— Experimental curves at 25° (○), 15° (●), 5·75° (◑), and 0° (⊗).
– – – Theoretical curve at 25°, calc. according to equation (4).

Influence of Temperature.—Measurements of initial rates of iodine consumption at various pH values and at temperatures from 0° to 25° show that the reaction has an apparent activation energy of 8·0 kcal. mole^{-1}. This value is apparently independent of pH within the range studied (12·5—14·0).

DISCUSSION

An alkaline solution of iodine containing potassium iodide contains initially the species, I_2, I_3^-, HIO, and IO^-, and any or all of these may be the active entity responsible for the oxidation of formaldehyde. From the equilibrium constants for the reactions:

$$I_2 + H_2O \overset{K_1}{\rightleftharpoons} HIO + I^- + H^+ \qquad (K_1 = 5{\cdot}4 \times 10^{-13}) \quad \text{(ref. 6)}$$

$$I_2 + I^- \overset{K_2}{\rightleftharpoons} I_3^- \qquad (K_2 = 1{\cdot}36 \times 10^{-3}) \quad \text{(ref. 7)}$$

$$HIO \overset{K_3}{\rightleftharpoons} H^+ + IO^- \qquad (K_3 = 4{\cdot}5 \times 10^{-13}) \quad \text{(ref. 8)}$$

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[5] Bartlett, *J. Amer. Chem. Soc.*, 1934, **56**, 967; Bell and Lidwell, *Proc. Roy. Soc.*, 1940, *A*, **176**, 88; Bell and Longuet-Higgins, *J.*, 1946, 636.

[6] Allen and Keefer, *J. Amer. Chem. Soc.*, 1955, **77**, 2957.

[7] Jakowkin, *Z. phys. Chem.*, 1894, **13**, 539.

[8] Skrabal, *Ber.*, 1942, **75**, 1570.

it is possible to calculate the concentrations of the different species present at 25° and at various pH values in a solution containing 0·0075 mole of potassium iodide per litre. It is unlikely that the iodine molecule or the tri-iodide ion plays a significant part in the reaction since towards the neutral pH region (where the concentrations of these species are relatively high) the rate of oxidation of formaldehyde is very small. The values of [HIO] and $[IO^-]$ depend, of course, on the value adopted for the dissociation constant of hypoiodous acid; of the three values available [8-10] that due to Skrabal [8] has been chosen here since it is in good agreement with the dissociation constants for the other hypohalous acids.

In aqueous solutions containing less than 2% of formaldehyde, the available evidence strongly suggests that the aldehyde, although completely monomeric,[11] is present almost entirely as the monohydrate, methanediol. This conclusion is based on studies of the absorption spectrum [12] and Raman spectrum [13] of formaldehyde solutions which show carbonyl groups to be absent, and on vapour-pressure measurements [14] which indicate that in dilute aqueous solution formaldehyde exists predominantly in the hydrated form. The acid dissociation constant of methanediol has been determined by several workers,[15] and the most recent value has been adopted in this work. The variation with pH at the temperatures used of $[CH_2(OH)_2]$ and $[CH_2(OH)\cdot O^-]$ may readily be determined and it is found that both species exist in appreciable concentration in the pH range used for kinetic studies.

The observed dependence of rate on formaldehyde and iodine concentrations (Figs. 1 and 2) presumably indicates the occurrence of binary reactions involving species whose concentrations at any given pH and temperature are directly proportional to the total concentrations of aldehyde and halogen present. Since the most likely reactive entities are, on the one hand, methanediol and the derived hydroxymethoxyl and, on the other, hypoiodous acid and the hypoiodite ion, the following equation will in general represent the overall rate of reaction:

$$-\frac{d[I_2]}{dt} = r = k_1[CH_2(OH)_2][HIO] + k_2[CH_2(OH)_2][IO^-] + k_3[CH_2(OH)\cdot O^-][HIO] + k_4[CH_2(OH)\cdot O^-][IO^-]. \quad (1)$$

If $[CH_2(OH)_2] = x$ and $[CH_2(OH)_2] + [CH_2(OH)\cdot O^-] = a$,

then $$r = k_1[HIO] + k_2x[IO^-] + k_3(a - x)[HIO] + k_4(a - x)[IO^-]; \quad (2)$$

whence $$\frac{r}{[IO^-]} = x\left(k_2 - k_4 + k_1\frac{[HIO]}{[IO^-]} - k_3\frac{[HIO]}{[IO^-]}\right) + a\left(k_4 + k_3\frac{[HIO]}{[IO^-]}\right). \quad (3)$$

Now, from the experimentally determined relation between rate and pH at 25° (Fig. 3) and from the dissociation constants of methanediol and hypoiodous acid at this temperature, it is possible to plot $r/[IO^-]$ against x; this is shown in Fig. 4. At very high pH values, where x is small, $[HIO]/[IO^-]$ will also be small. Thus under these conditions the slope of the resulting linear part of the graph in Fig. 4 will, as an approximation, be equal to $(k_2 - k_4)$ and the intercept on the ordinate will be k_4a. From these quantities, it is found that $k_2 = 0\cdot4$ l. mole^{-1} sec.$^{-1}$, and $k_4 = 12\cdot4$ l. mole^{-1} sec.$^{-1}$.

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[9] Fürth, *Z. Elektrochem.*, 1922, **28**, 51.

[10] Josien and Sourisseau, *Bull. Soc. chim. France*, 1950, 255.

[11] Auerbach and Barschall, " Studien über Formaldehyd. Part I. Formaldehyd in wässriger Lösung," Julius Springer, Berlin, 1905, p. 10.

[12] Schou, *Compt. rend.*, 1928, **186**, 690; *J. Chim. phys.*, 1929, **26**, 72; Bieber and Trümpler, *Helv. Chim. Acta*, 1947, **30**, 1860.

[13] Hibben, *J. Amer. Chem. Soc.*, 1931, **53**, 2418; Trumpy, *Kgl. norske Videnskab. Selskab Skrifter*, 1935, **9**, 1.

[14] Blair and Ledbury, *J.*, 1925, **127**, 26; Ledbury and Blair, *J.*, 1925, **127**, 2832; Walker, *J. Phys. Chem.*, 1931, **35**, 1104.

[15] Euler, *Ber.*, 1905, **38**, 255; Euler and Lovgren, *Z. anorg. Chem.*, 1925, **147**, 123; Wadano, *Ber.*, 1934, **67**, 191; Martin, *Austral. J. Chem.*, 1954, **7**, 400; Bell and McTigue, *J.*, 1960, 2983.

Theoretically it should be possible to substitute the above values for k_2 and k_4 into equation (1) and thus determine k_1 and k_3 by solution of the simultaneous equations obtained at two different pH values. This is not possible in practice, however, since the uncertainty regarding the concentrations of hypoiodous acid and the hypoiodite ion causes a considerable error. As an approximation, therefore, it has been assumed that, at pH 10, the terms on the right-hand side of equation (1) involving either hydroxymethoxyl ion or hypoiodite ion will disappear. From the observed value of the rate of iodine consumption under these conditions, it is found that $k_1 \approx 0{\cdot}8$ l. mole^{-1} sec.$^{-1}$.

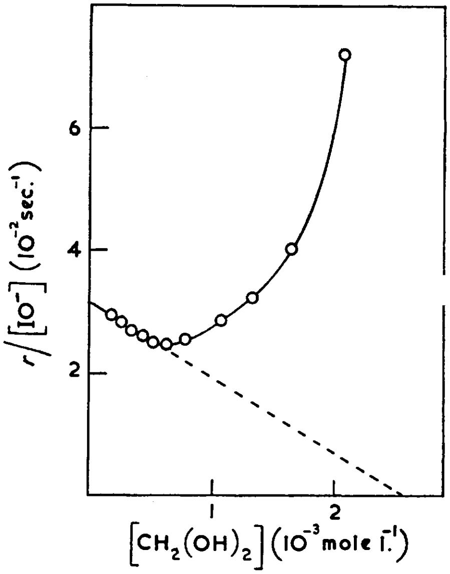

FIG. 4. The reaction of formaldehyde with iodine and alkali.
Temp. = 25°; [Formaldehyde] = 0·0025M; [Iodine] = 0·0051M.

The remaining velocity constant, k_3, may then be readily calculated and the average value found from measurements at four different pH values is $k_3 \approx 50$ l. mole^{-1} sec.$^{-1}$.

The total rate of iodine consumption (in mole l.$^{-1}$ sec.$^{-1}$) should thus be given by the equation:

$$-\frac{d[I_2]}{dt} = 0{\cdot}8[CH_2(OH)_2][HIO] + 0{\cdot}4[CH_2(OH)_2][IO^-] + 50[CH_2(OH){\cdot}O^-][HIO] + 12{\cdot}4[CH_2(OH){\cdot}O^-][IO^-]. \quad (4)$$

From the dissociation constants of methanediol and hypoiodous acid at 25°, the concentrations of the various species present at different pH values may readily be calculated, and substitution of these into equation (4) gives the rate at any given pH. The resulting theoretical curve of rate against pH (in which rates are now expressed as moles of iodine consumed per mole of formaldehyde per second) is shown in Fig. 3, together with the corresponding experimental curve obtained at the same temperature. This provides a check of the essential correctness of the values adopted for the individual velocity constants, for not only are the two curves of similar form but also the calculated and experimental values of the rate are in reasonably close agreement over the whole range of pH investigated.

Although, owing to the various assumptions made, the values of k_1, k_2, k_3, and k_4 are only approximate, they undoubtedly indicate the probable relative importance of the various possible binary reactions taking place. It thus appears that the hydroxymethoxyl ion is more reactive than the methanediol molecule, but that the hypoiodous acid molecule is more reactive than the hypoiodite ion. Apart from the various reactions of these species with one another to yield formic acid and iodide ions, proton-transfer processes of the type:

$$CH_2(OH)_2 + IO^- \longrightarrow CH_2(OH){\cdot}O^- + HIO$$

and

$$CH_2(OH){\cdot}O^- + HIO \longrightarrow CH_2(OH)_2 + IO^-$$

may well also occur, but no information is obtainable about such reactions from the kinetic results.

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