662. *Quantitative Aspects of the Base-catalysed Reaction of Aliphatic Aldehydes with Iodine. Part II.*[1] *Acetaldehyde and Propionaldehyde.*

By C. F. Cullis and P. A. Swain.

Acetaldehyde and propionaldehyde undergo two distinct reactions with iodine in alkaline solution, namely, direct oxidation to the corresponding acid and substitution leading to organic iodo-compounds. Determinations have been made under a wide range of experimental conditions of the fate of the consumed iodine, and fatty acids, iodo-acids, and organically bound iodine have been estimated quantitatively. Both the extent and the rate of iodine consumption are influenced by the concentration and order of mixing of the reactants and by the pH. Kinetic measurements show that the rate of consumption of iodine by acetaldehyde and propionaldehyde is given by an equation of the form:

$$-d[I_2]/dt = k_1[\text{HIO}][\text{Aldehyde}] + k_2[\text{OH}^-][\text{Aldehyde}].$$

The first term represents the rate of oxidation of the aldehyde to a carboxylic acid, and the second term represents the rate of enolisation of the aldehyde which is the rate-determining step in the substitution.

IN Part I, a kinetic study was reported of the base-catalysed reaction of iodine with formaldehyde,[1] which over a wide range of pH was thus quantitatively oxidised to formic

[1] Part I, Cullis and Swain, *J.*, 1962, 2228.

acid.[2] The present paper describes some work on the corresponding reaction with acetaldehyde and propionaldehyde. Acetaldehyde can react with alkaline iodine solutions in two distinct ways;[3] on the one hand, it may undergo the iodoform reaction and on the other it may be oxidised directly to acetic acid. The present investigation enables some of the kinetic features of the two processes occurring with both acetaldehyde and propionaldehyde to be elucidated.

EXPERIMENTAL

Materials.—The purest available commercial samples of acetaldehyde and propionaldehyde were fractionally distilled in a current of nitrogen; middle fractions were collected (and stored in blackened flasks to prevent photodecomposition[4]) and their purities were checked by measurement of the b. p. and refractive index. Standard solutions were prepared gravimetrically,[5] since conventional standardisation procedures were unsatisfactory. Newly prepared aldehyde solutions gave reproducible results for only about three days and fresh solutions were made up every two days.

All other reagents were of " AnalaR " grade and were further purified where necessary by standard methods.

Preparation of Buffer Solutions and Measurement of pH.—The range of buffer solutions used and the method of measurement of pH have been described in Part I.

Kinetic Measurements.—Since the reactions being studied were relatively rapid even at 0°, rate measurements were made in Y-tubes. In order to minimise disproportionation of hypoiodite and the aldol-type of condensation which aliphatic aldehydes undergo in alkaline solution (cf. Fig. 4), the iodine and aldehyde solutions were placed initially in one limb and the aqueous alkali or buffer solution was placed in the other; control experiments confirmed that neither acetaldehyde nor propionaldehyde reacts with iodine in neutral solution. The reaction was started by rapid mixing of the contents of the two limbs and was stopped by pouring the reacting solutions into a slight excess of hydrochloric acid. The liberated iodine was then immediately titrated with thiosulphate.

Aliquot parts of the resulting solutions were analysed for selected individual compounds and classes of compounds, and the following analytical procedures were employed.

Qualitative Analysis.—(a) *Fatty acids and iodo-acids.* Organic acids were extracted with ether, and the combined ethereal extracts were washed with concentrated aqueous ammonia. The anions of fatty acids and iodo-acids in the ammoniacal solution were identified by paper chromatography.[6]

(b) *Formaldehyde and formic acid.* The presence of formaldehyde was investigated by means of its colour reaction with chromotropic acid[7] but this compound itself was never detected. The mixture was also treated with magnesium turnings and concentrated hydrochloric acid; this reduces any formic acid to formaldehyde,[8] and the test described above may then be applied.

Quantitative Analysis.—(a) *Organic acids.* Attempts were made to extract organic acids into ether, treat the combined ethereal extracts with a known volume of standard borax solution, and determine by acid–base titration the amount of unchanged borax and hence the quantity of acid which has reacted with it. Unfortunately, however, acetic acid and propionic acid are too soluble in water to be extracted even approximately quantitatively into ether.

(b) *Organically bound iodine.* Both acid and neutral organic iodine compounds were readily extracted with ether, and the total iodine content was determined by reduction to iodide, a modification of the sodium–alcohol method[9] being used. Neutral organic iodine compounds alone were extracted into ether from an alkaline reaction mixture and iodo-acids then determined by difference.

[2] Romijn, *Z. analyt. Chem.*, 1897, **36**, 18; Hatcher and Mueller, *Trans. Roy. Soc. Canada*, 1929, **23**, 35.

[3] Sno-Chow Woo and Tsinchang Chu, *Sci. Record*, 1949, **2**, 280; Bose, *J. Indian Chem. Soc.*, 1957, **34**, 739, 825.

[4] McNesby and Heller, *Chem. Rev.*, 1954, **54**, 325.

[5] Cf. Goodwin, *J. Amer. Chem. Soc.*, 1920, **42**, 39.

[6] Hashmi and Cullis, *Analyt. Chim. Acta*, 1956, **14**, 336.

[7] Bricker and Vail, *Analyt. Chem.*, 1950, **22**, 720.

[8] Droller, *Z. physiol. Chem.*, 1932, **211**, 57; Grant, *Analyt. Chem.*, 1948, **20**, 267.

[9] Drogin and Rosanoff, *J. Amer. Chem. Soc.*, 1916, **38**, 711.

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(c) *Iodoform.* Organic constituents were extracted into chloroform, and the resulting solution was carefully dried. The concentration of iodoform in the chloroform layer was determined spectrophotometrically.[10]

(d) *Propionaldehyde.* Organic compounds were extracted into ether. Aldehydes were transferred quantitatively from the ether layer by shaking the latter with aqueous sodium hydrogen sulphite, and the concentration of combined propionaldehyde in the resulting extract was determined by a modification of a colorimetric method.[11]

RESULTS

Kinetic Measurements.—The majority of rate measurements were carried out at 0°. At this temperature and within the range of reactant concentrations used, consumption of iodine
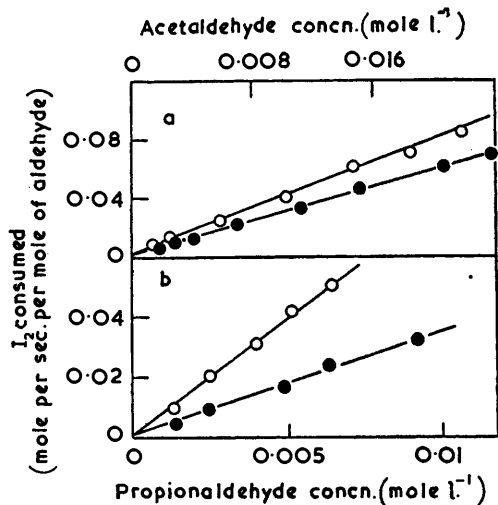

FIG. 1. The influence of aldehyde concentration on the rate of iodine consumption at 0°.
(a) [Iodine] = 0·0051M.   O, pH = 12·70; ●, pH = 12·86.
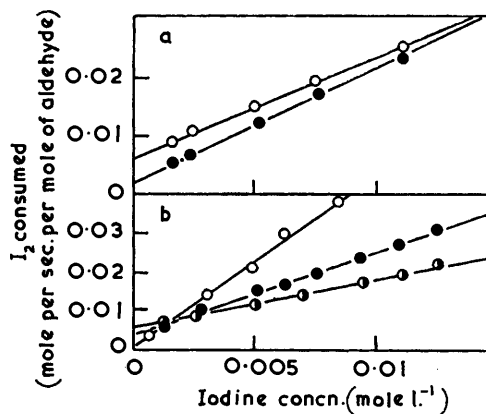(b) [Iodine] = 0·0051M.   O, pH = 12·60; ●, pH = 11·30.

FIG. 2. The influence of iodine concentration on the rate of iodine consumption at 0°.
(a) [Acetaldehyde] = 0·0025M.   O, pH = 13·43; ●, pH = 12·42.
(b) [Propionaldehyde] = 0·0025M.   O, pH = 12·60; O, pH = 13·00; ◐, pH = 13·50.

by acetaldehyde and propionaldehyde is generally complete within about 10 min. but reaction was slow enough to enable the initial rate of disappearance of iodine to be determined accurately. With both compounds the reaction is of the first order with respect to the aldehyde (Fig. 1). On the other hand, plots of initial rate against iodine concentration, although linear, do not pass through the origin (Fig. 2); this may perhaps indicate the simultaneous occurrence of two reactions, one of which is of the first order, and the other of zero order, with respect to the halogen.

The influence of pH on the rate of consumption of iodine may be seen from Fig. 3, in which each point shown is the mean of at least three rate determinations. The shape of the curves obtained suggests that they may result from the superposition of two different rate curves which in turn implies the operation of two distinct mechanisms according to the pH of the system.

The initial rates of iodine consumption shown will not, however, be proportional to the rates of disappearance of the aldehydes since the amount of iodine consumed varies considerably with pH (cf. Fig. 5). A closer approximation to the true rates of disappearance of the aldehydes may be obtained by dividing the overall rate of iodine uptake at each pH by the total iodine consumption at that pH. The main effect of such a correction is to reduce the values

[10] Dal Nogare, Norris, and Mitchell, *Analyt. Chem.*, 1951, **23**, 1473.
[11] Jones and Riddick, *Analyt. Chem.*, 1954, **26**, 1035.

of the initial rate in the region of high pH, but the general shape of the rate–pH curve is not substantially altered. In fact the true rates of disappearance of the aldehydes could only be calculated if the relative extents of their two concurrent reactions with iodine were known.

Total Iodine Consumption.—The number of moles of iodine consumed per mole of aldehyde is influenced by a variety of factors. One of these is the order of mixing of the reactants. In general, the longer the time for which either the iodine + alkali or the aldehyde + alkali are " pre-mixed " before the third component is added, the lower is the iodine uptake. Fig. 4 shows the results of some typical experiments in which propionaldehyde and alkali were set aside for varying times before the iodine was added and it will be seen that the higher the pH
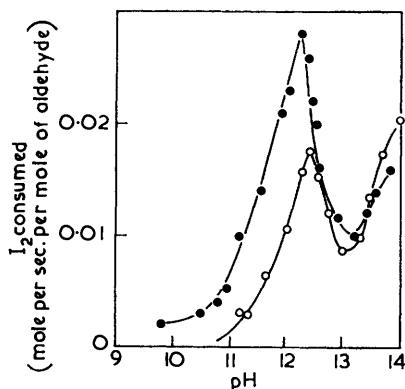

FIG. 3. The influence of pH on the rate of iodine consumption at 0°.

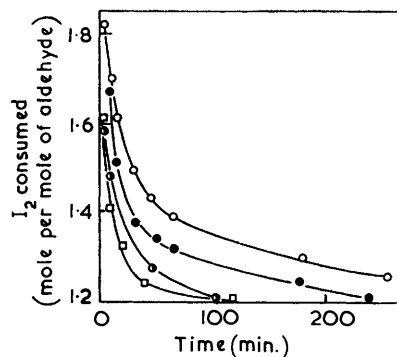[Iodine] = 0·0051M; ○, [Acetaldehyde] = 0·0025M; ●, [Propionaldehyde] = 0·0025M.

Fig. 4. The influence of the time for which propionaldehyde and alkali solutions were " pre-mixed " on maximum iodine consumption at 25°.

[Propionaldehyde] = 0·0025M; [Iodine] = 0·0051M. ○, pH = 13·10; ●, pH = 13·40; ◑, pH = 13·60; □, pH = 14·00.

the more pronounced is this effect; a similar but less well-defined influence was apparent with acetaldehyde. In all subsequent measurements of overall consumption of iodine, therefore, the alkali solution was added to the " pre-mixed " iodine + aldehyde solution. Under these conditions the total uptake of iodine increases with pH until a steady value is reached at a pH of *ca.* 13·4; with both acetaldehyde and propionaldehyde the maximum consumption of iodine is almost exactly equivalent to two moles of iodine per mole of aldehyde (Fig. 5). The amount of halogen consumed at first increases with initial iodine concentration; if, however, a considerable excess of iodine is used, the overall consumption decreases slightly (Fig. 6).

Identification of Acid Products.—Experiments were carried out at several different initial pH values (Table 1). With acetaldehyde, these show that acetic (or formic) acid is the only

TABLE 1.

Acids formed in the base-catalysed iodination of acetaldehyde and propionaldehyde.

Temp. = 25°; [Aldehyde] = 0·0025M; [Iodine] = 0·0051M.

pH	Acids formed from acetaldehyde		Acids formed from propionaldehyde	
	Fatty acids	Iodo-acids	Fatty acids	Iodo-acids
11·5	Acetic (or formic) 0·38 (0·39)	None	—	—
12·0	Acetic (or formic) 0·38 (0·39)	None	—	—
12·5	Acetic (or formic) 0·38 (0·39)	None	Propionic 0·50 (0·49)	α(or β)-Iodopropionic 0·55 (0·55)
13·0	Acetic (or formic) 0·38 (0·39)	None	Propionic 0·50 (0·49)	α(or β)-Iodopropionic 0·55 (0·55)
13·5	None	None	Propionic 0·51 (0·49)	α(or β)-Iodopropionic 0·56 (0·55)

R_F values of acids present in products are given together with the corresponding values determined for the known acids in parentheses.

acid formed; the method used does not unfortunately distinguish between these two compounds. Since formic acid is scarcely extracted from aqueous solution by ether, however, the acid " spots " observed are presumably due to acetic acid. This compound could not, however, be detected above pH 13·5. With propionaldehyde, both propionic acid and an iodopropionic acid are formed at all pH values investigated.

Tests showed that formic acid was present above pH 13 in the reaction products of the acetaldehyde + iodine reaction. Positive results were also obtained above pH 13·5 in the corresponding experiments with propionaldehyde, but here only if at least 30 minutes elapsed between the start of the reaction and the analysis of products.
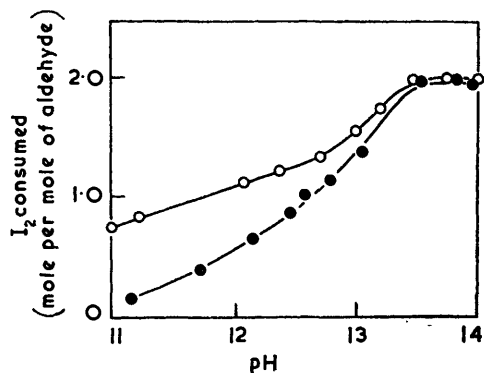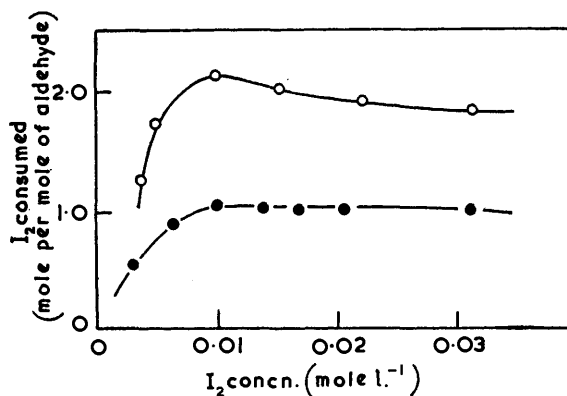

FIG. 5. The influence of pH on maximum iodine consumption at 25°.

[Iodine] = 0·0051M; ○, [Acetaldehyde] = 0·0025M; ●, [Propionaldehyde] = 0·0025M.

FIG. 6. The influence of iodine concentration on maximum consumption of acetaldehyde at 25°.
[Acetaldehyde] = 0·0025M; [Iodine] = 0·0051M; ○, pH = 13·35; ●, pH = 11·36.

Quantitative Analysis of Initial Reactants.—Solutions containing propionaldehyde and iodine were analysed after various reaction times and at different pH values for any unchanged aldehyde. The results in Table 2 show that the propionaldehyde is completely consumed except at low pH values.

TABLE 2.

Spectrophotometric analysis of residual propionaldehyde.

Temp. = 25°; [Propionaldehyde] = 0·0025M; [Iodine] = 0·0051M.

| pH	Reaction time (min.)	Et·CHO remaining (%)	Reaction time (min.)	Et·CHO remaining (%)
8·8	30	5	180	0
9·4	30	2·5	180	0
11·3 or 11·8	30	0	—	—

Quantitative Analysis of Products.—(a) *Organic acids.* Although it was not possible to obtain reliable results for the total amounts of organic acids formed (see p. 3349), such measurements nevertheless show that the amounts of acetic and propionic acid formed at first increase with pH, acquiring a maximum value at pH *ca.* 12·5 and then decrease quite sharply as the solution is made more alkaline.

(b) *Organically bound iodine.* Fig. 7 shows the different fates of the halogen consumed by the two aldehydes. With acetaldehyde (Fig. 7a), the quantity of iodine converted into an organic form not only increases with pH but also forms a progressively larger proportion of the total halogen consumed (cf. Fig. 5). Since iodo-acids are absent (Table 1) and only

FIG. 7. The influence of pH on the amount of organically bound iodine in the products.

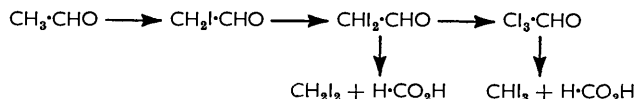Temp. = 25°; [Aldehyde] = 0·0025M; [Iodine] = 0·0051M.

(a) ○, Total organically bound iodine; ◑, iodine present as iodoform; – – – –, iodine believed to be present as methylene iodide.
(b) ○, Total organically bound iodine; ●, iodine present in neutral organic form; ◑, iodine present as iodoform; – – – –, iodine believed to be present as methylene iodide; — · — · —, iodine present as iodo-acids.
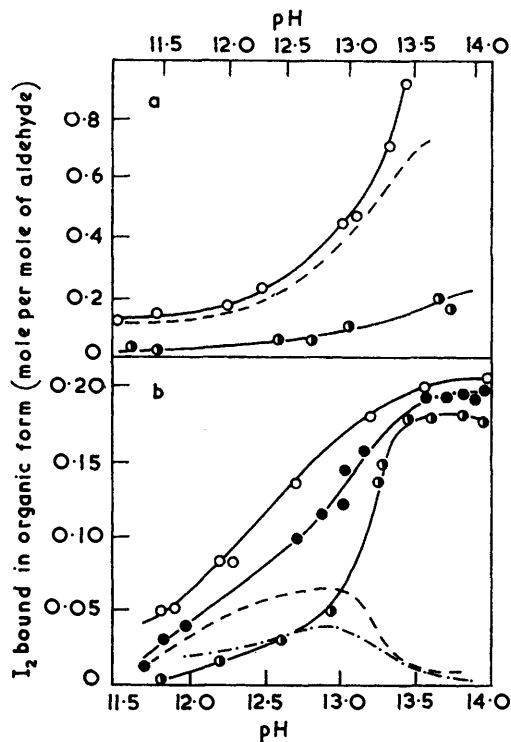
relatively small amounts of iodoform are formed (Fig. 7a), the major part of the organically bound iodine must be present as other neutral iodo-compounds. With propionaldehyde (Fig. 7b), the results are generally similar but show that a somewhat greater proportion of the iodine converted into organic form can be accounted for as iodoform and that correspondingly smaller amounts of other neutral iodo-compounds are therefore formed. The difference between the total organically bound halogen and that present in neutral forms gives a measure of the amounts of iodo-acids formed; these are found to be appreciable.

DISCUSSION

Reactions of Acetaldehyde.—The observed variation of rate with pH (Fig. 3) suggests that at least two reactions can take place between acetaldehyde and iodine in alkaline solution. Since at the highest pH values, acetic acid is absent and the amount of organically bound iodine is a maximum, substitution reactions, such as the iodoform reaction, presumably predominate in these conditions. Iodoform itself does not account for more than a small part of the iodine converted into organic form and, since no iodo-acids are detectable, the residual organically bound iodine is, by analogy with methyl ketones,[12] probably present as methylene iodide, formed by the premature hydrolysis of di-iodo-acetaldehyde:

$$CH_3 \cdot CHO \longrightarrow CH_2I \cdot CHO \longrightarrow CHI_2 \cdot CHO \longrightarrow CI_3 \cdot CHO$$

$$CH_2I_2 + H \cdot CO_2H \qquad CHI_3 + H \cdot CO_2H$$

[12] Cullis and Hashmi, *J.*, 1956, 2512.

The broken line in Fig. 7a represents methylene iodide formation, calculated on the assumption that this is the only iodinated organic product other than iodoform.

The formation of one mol. of iodoform and methylene iodide from acetaldehyde requires the consumption of three and two mol. of iodine, respectively, and if these are the only two organic iodo-compounds produced the total amount of iodine used in their formation
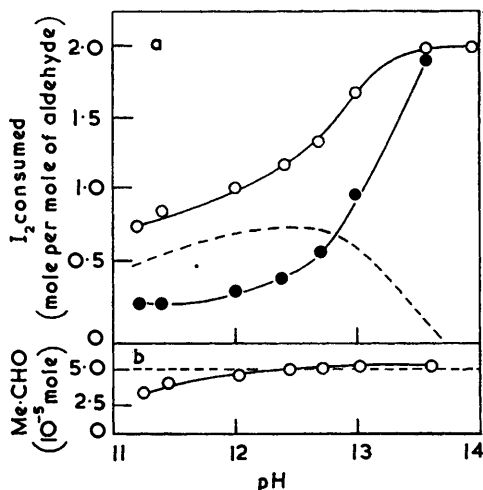

Fig. 8. The influence of pH on the two competing reactions of alkaline iodine with acetaldehyde and on the total consumption of acetaldehyde.

Temp. $= 25°$; [Acetaldehyde] $= 0.0025$M; [Iodine] $= 0.0051$M.

(a) ○, Total iodine consumed; ●, iodine consumed in formation of iodoform and methylene iodide; – – – –, iodine believed to be consumed in formation of acetic acid.

(b) ○, Acetaldehyde consumed in formation of products shown in Fig. 8a; – – – –, acetaldehyde present initially.

can be calculated. This is shown in Fig. 8a, together with the overall iodine uptake. The difference between these two quantities presumably represents the iodine consumed in the straight oxidation of acetaldehyde:

$$CH_3 \cdot CHO + I_2 + 2NaOH \longrightarrow CH_3 \cdot CO_2H + 2NaI + H_2O$$
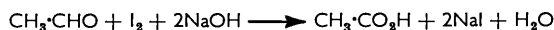
and the broken line in Fig. 8a is the resulting theoretical curve for acetic acid, which is similar in shape to that obtained during attempts to determine this product directly. If the total amount of acetaldehyde needed to form the three products, as shown in Fig. 8a, is compared with the quantity present initially in the system, all the aldehyde can, except at low pH values, be accounted for completely (Fig. 8b). Direct oxidation and substitution thus both occur to extents dependent on the pH, and the former process, which predominates at pH 11—13, gives way to the latter in more strongly alkaline conditions.

The formation of acetic acid reaches a maximum at a pH where the concentration of hypoiodous acid is also a maximum,[13] suggesting that the undissociated hypoiodous acid molecule is the species responsible for oxidation. Since the consumption of iodine by acetaldehyde is always of the first order with respect to aldehyde (Fig. 2a), the direct oxidation to acetic acid would be expected to obey the kinetic law:

$$d[CH_3 \cdot CO_2H]/dt = k_1[HIO][CH_3 \cdot CHO].$$

In the iodoform and related substitution reactions, the formation of the enolate ion is the rate-determining step,[14] and the kinetic equation is of the form:

$$d[\text{Subst. products}]/dt = k_2[OH^-][CH_3 \cdot CHO].$$

The total rate of reaction will thus be given by:

$$-d[I_2]/dt = k_1[HIO][CH_3 \cdot CHO] + k_2[OH^-][CH_3 \cdot CHO].$$
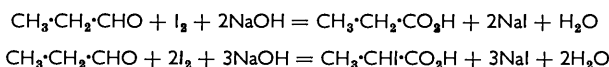
[13] Cf. Ingles and Israel, *J.*, 1948, 810.
[14] Bartlett, *J. Amer. Chem. Soc.*, 1934, **56**, 967; Bell and Longuet-Higgins, *J.*, 1946, 636.

Since at a given pH, $[HIO] \propto [I_2]$, approximate values for k_1 and k_2 may be found from measurements of the slope and intercept of plots of initial rate against iodine concentration (Fig. 2a), and these are shown in Table 3.
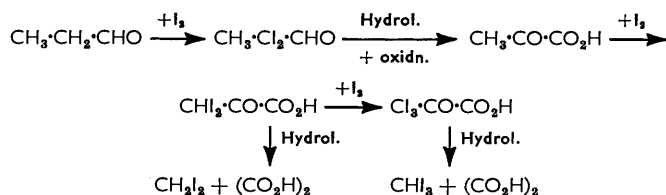
TABLE 3.

Velocity constants for oxidation and substitution at 0°.

Aldehyde	k_1 or k_1' (l. mole⁻¹ sec.⁻¹)	k_2 or k_2' (l. mole⁻¹ sec.⁻¹)
Acetaldehyde	2	0·06
Propionaldehyde	6	0·02

Reactions of Propionaldehyde.—Propionaldehyde, on treatment with alkaline iodine, yields both the oxidation product, propionic acid, and some neutral substitution products. The concentration of propionic acid reaches a maximum at pH 12·4 and falls as the pH is further increased. An appreciable amount of an iodo-acid (probably α-iodopropionic acid, formed by oxidation of the corresponding iodo-aldehyde rather than by iodination of propionic acid [12]) is also produced and its concentration follows a similar variation with pH. The overall equations representing the formation of these acid products are:

$$CH_3 \cdot CH_2 \cdot CHO + I_2 + 2NaOH = CH_3 \cdot CH_2 \cdot CO_2H + 2NaI + H_2O$$

$$CH_3 \cdot CH_2 \cdot CHO + 2I_2 + 3NaOH = CH_3 \cdot CHI \cdot CO_2H + 3NaI + 2H_2O$$

The neutral iodo-compounds, which become the predominant products at high pH values, are probably formed by iodination at the α-position in propionaldehyde, followed by hydrolysis and oxidation to pyruvic acid. This compound is known [15] to yield iodoform and oxalic acid, and as a result of premature fission of the di-iodo-compound also appears to give some methylene iodide: *

Thus the following overall equations represent the changes taking place:

$$CH_3 \cdot CH_2 \cdot CHO + 5I_2 + 8NaOH = CH_2I_2 + (CO_2H)_2 + 8NaI + 5H_2O$$

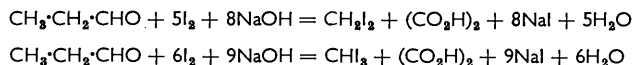$$CH_3 \cdot CH_2 \cdot CHO + 6I_2 + 9NaOH = CHI_3 + (CO_2H)_2 + 9NaI + 6H_2O$$

Table 4 shows the calculated amounts of iodine used in forming each of these reaction products, and the sum of these is in good agreement with the measured total iodine consumption at all pH values investigated. In contrast, the theoretical quantity of propionaldehyde consumed in these reactions is considerably smaller than the amount added initially. Since no aldehyde remains unchanged at the end of the reaction, considerable polymerisation must also occur and this conclusion is supported by the results shown in Fig. 4.

The kinetic relations observed with propionaldehyde are closely similar to those found for acetaldehyde. The rate of reaction may therefore be represented by an equation of the form:

$$-d[I_2]/dt = k_1'[HIO][CH_3 \cdot CH_2 \cdot CHO] + k_2'[OH^-][CH_3 \cdot CH_2 \cdot CHO]$$

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* This compound has been shown to be hydrolysed slowly in the existing experimental conditions and is no doubt the source of the formic acid detected at high pH values.

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

TABLE 4.

Influence of pH on the products formed from propionaldehyde.

Temp. = 25°; [Propionaldehyde] = 0·0025M; [Iodine] = 0·0051M.

	Iodine (10^{-5} mole) consumed in forming:				Total iodine consumed (calc.) (10^{-5} mole)	Total iodine consumed (expt.) (10^{-5} mole)	Total aldehyde consumed (calc.) (10^{-5} mole)	Total aldehyde present (10^{-5} mole)
pH	Et·CO$_2$H	C$_2$H$_4$I·CO$_2$H	CHI$_3$	CH$_2$I$_2$				
12·1	1·75	0·18	0·20	1·00	3·13	3·00	2·16	5·00
12·2	2·40	0·20	0·28	1·10	3·98	4·00	2·87	5·00
12·4	3·30	0·32	0·40	1·30	5·32	5·00	3·95	5·00
12·6	2·85	0·36	0·57	1·60	5·38	5·50	3·54	5·00
13·0	1·70	0·28	1·20	4·00	7·18	7·50	2·98	5·00
13·2	1·40	0·20	2·12	4·70	8·42	8·50	2·89	5·00
13·4	1·25	0·12	3·24	5·00	9·61	9·50	2·91	5·00
13·8	1·13	None	3·60	5·50	10·22	10·00	2·80	5·00
14·0	1·10	None	3·60	5·60	10·30	10·00	2·82	5·00

where k_1' is a composite velocity constant representing direct oxidation processes and k_2' is the velocity constant for the enolisation of the aldehyde.

An average value for k_2' may be determined from the intercepts of the plots shown in Fig. 2b, and a value for k_1' may then be obtained by direct substitution into the above equation of values for all the other quantities; this substitution is best carried out for low pH values (*i.e.*, between 11 and 12), so that the concentration of the keto-form of propionaldehyde is as nearly as possible equal to the total concentration of aldehyde added. The resulting approximate values for k_1' and k_2' are given in Table 3.

General Conclusions.—The alkaline iodination of acetaldehyde and propionaldehyde may involve both straight oxidation to the corresponding carboxylic acids and direct substitution to yield products which eventually suffer hydrolysis.

The straight oxidation appears to involve a bimolecular reaction between the hypoiodous acid molecule and the keto-form of the aldehydes, and the results in Table 3 (which owing to the asumptions made in their derivation must be regarded as only semiquantitative) show that acetaldehyde undergoes this type of process less readily than does propionaldehyde. The reaction probably takes place as follows:
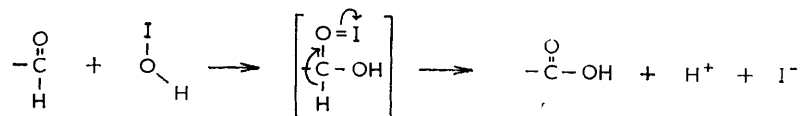
and the greater positive inductive effect of ethyl than of methyl will result in a greater polarisation of the C=O group in propionaldehyde.

The rate-determining step in the substitution is the formation of the enolate ion, and no information can thus be obtained from kinetic studies as to the nature of the iodinating species. The first stage in the formation of this ion (the removal of a proton) should occur more readily with acetaldehyde which has no methyl groups attached to the α-carbon atom. On the other hand, the presence of a methyl group in the enolate ion formed from propionaldehyde will exert a stabilising influence, since this group can hyperconjugate with the double bond.[16] On account of these two opposing factors, it is difficult to draw conclusions about the relative extents of enolisation of the two aldehydes, but the results in Table 3, which illustrate the greater tendency of acetaldehyde to undergo substitution, suggest that the former factor is the more important.

[16] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Limited, London 1953, p. 90.