77. *Reactions of the Cobaltic Ion. Part III. The Kinetics of the Reactions of the Cobaltic Ion with Aldehydes and Alcohols.*

By C. E. H. Bawn and A. G. White.

The preliminary results of a study of the reactions of the cobaltic ion with formaldehyde and methyl, ethyl, and *n*-propyl alcohols in aqueous 5N- and 10N-sulphuric acid are summarised. The rate equations have been determined in each case, and various mechanisms for the reactions are discussed. In general the results would appear to be consistent with the assumption that the first step is an electron-transfer reaction between the cobaltic ion and the organic compound with the generation of a free radical. The secondary reactions of the various types of free radicals thus formed are discussed.

In the preceding paper the powerful oxidising action of the cobaltic ion towards a wide variety of organic compounds was summarised, and in particular a detailed kinetic study of the oxidation of formic acid was reported. In the present paper this work has been extended to other simple organic molecules, and the preliminary results of the reactions of the cobaltic ion with formaldehyde and the simple alcohols are summarised. Although it has not yet been possible to determine the reaction mechanism with the degree of completeness achieved with formic acid the results are consistent with the view that the primary reaction is an electron-transfer reaction between the cobaltic ion and the organic molecule with the formation of a formyl or alkoxyl radical.

EXPERIMENTAL.

Materials.—All reagents used, with the exception of cobaltic sulphate, were of " AnalaR " grade, and no further purification was attempted. The cobaltic sulphate was prepared as described in the preceding paper.

Kinetic Measurements.—These were carried out in 5N- or 10N-sulphuric acid to suppress the reaction of the cobaltic ion with water and permit a study of the reaction with the organic compound alone. The runs were always carried out in the presence of a considerable excess of the organic compound so that its concentration could be regarded as constant, and were followed by determination of the cobaltic-ion concentration in the reaction mixture by the titration methods described in Parts I and II (*J.*, 1951, 331, 339). Where the reaction proceeded too rapidly for the normal method of sampling to be used the reaction was carried out in a series of tubes, being started by addition of the organic compound to a tube and stopped by addition of excess of standard ferrous ammonium sulphate after a known time interval.

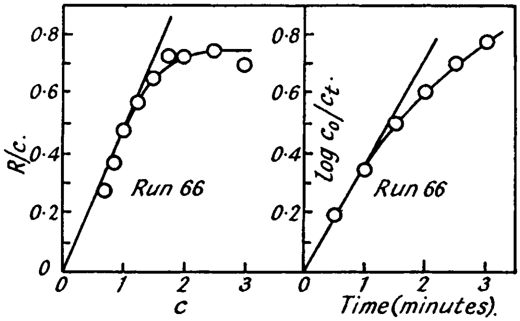
For runs above room temperature the reaction vessel was immersed in a bath with temperature thermostatically controlled to ±0·05°, while for runs between 0° and room temperature the reaction vessel was immersed in water, cooled to the appropriate temperature with ice, in a large Dewar vessel. By this latter means the temperature of the reaction mixture could be held constant, over the relatively short period required for a run, to within ±0·1°.

RESULTS.

Formaldehyde.—In the presence of a large excess of this compound the rate of disappearance of the cobaltic ion was neither of first- nor second-order form ([Co^{+++}] approximately 0·5 × 10^{-2}M.), and in order to determine the form of the overall rate equation the following method was used. Plots were prepared of the cobaltic-ion concentration (c) against time (t), and tangents drawn to these at selected values of c. The slope of the tangents thus gave the instantaneous rate of reaction (R) at that concentration. Finally R/c was plotted against concentration. It was found, as is shown by a typical plot in Fig. 1, that the reaction was of a variable order with respect to cobaltic-ion concentration, the overall rate being approximately of second order at low concentrations (*i.e.*, R/c proportional to concentration) and approximately of first order at high concentrations (*i.e.*, R/c independent of concentration). These facts may be satisfactorily accounted for by a rate equation * of the form

FIG. 1.

Reaction of the cobaltic ion and formaldehyde. Typical R/c against c and first-order plots.



$$-d[Co^{+++}]/dt = k_1[Co^{+++}]^2/(A + k_2[Co^{+++}])$$

for if at low concentration $A \gg k_2[Co^{+++}]$ it reduces to

$$-d[Co^{+++}]/dt = k_1[Co^{+++}]^2/A$$

while at high concentrations if $k_2[Co^{+++}] \gg A$ it reduces to

$$-d[Co^{+++}]/dt = k_1[Co^{+++}]/k_2$$

the order at intermediate concentrations being variable as was found experimentally. The values of k_1/k_2 and k_1/A were derived from the initial slopes of first order (*i.e.*, $\log_{10} c/t$) and R/c versus c plots, respectively. The initial portions of the first-order plots (*i.e.*, the high-concentration region) were

---

* An equation of the form $-d[Co^{+++}]/dt = k_1'[Co^{+++}] + k_2'[Co^{+++}]^2$ cannot account for the form of the $\frac{d[Co^{+++}]}{dt}\Big/[Co^{+++}]$ against [Co^{+++}] plot (Fig. 1).

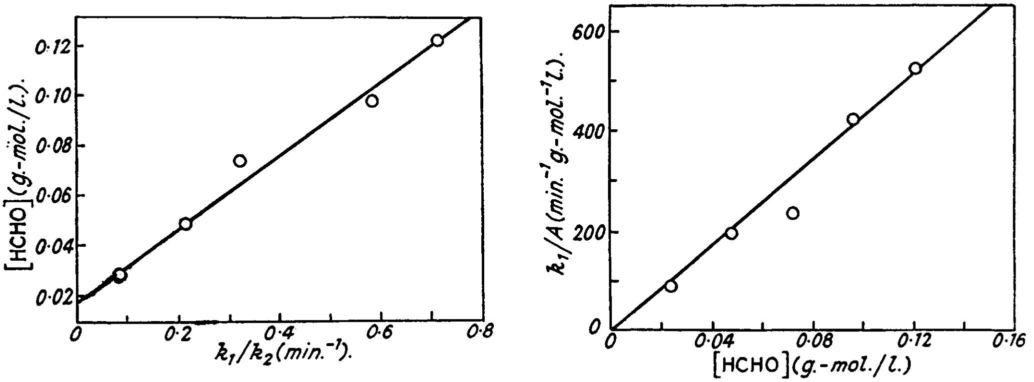
all found to be linear but the initial portions of R/c against c plots had in most cases to be obtained by extrapolation.

To determine the manner in which the formaldehyde concentration affected the rate, values of k_1/A and k_1/k_2 obtained at 0° for various formaldehyde concentrations were plotted against various functions of this concentration. It was found that both k_1/A and k_1/k_2 were proportional to the formaldehyde concentration, but the latter plot did not pass through the origin (Figs. 2*A* and 2*B*).

The results of experiments at constant formaldehyde concentration and different temperatures are presented in Fig. 3. In the limited temperature range over which it was possible to work (0—10°), the k_1/A plot was linear while that for k_1/k_2 was curved. The linearity of the k_1/A plot must imply either that A is temperature independent or that k_1 and A have approximately the same temperature coefficient.

FIG. 2*A*. FIG. 2*B*.

Reaction of cobaltic ion with formaldehyde in 5N-*sulphuric acid at* 0°.



Since formaldehyde reacts very rapidly with the cobaltic ion and its oxidation product formic acid reacts some 100 or more times more slowly it is very likely that in the presence of excess of formaldehyde the main product of oxidation is formic acid.

FIG. 3.

Effect of temperature on the reaction between cobaltic ion and formaldehyde in 5N-*sulphuric acid.*

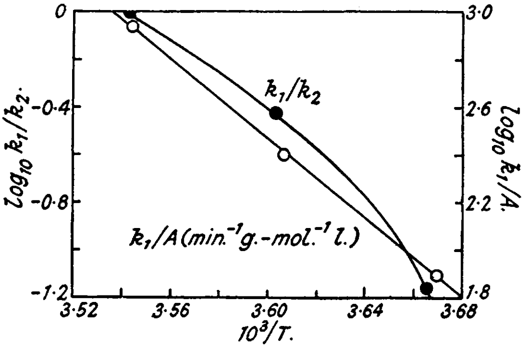
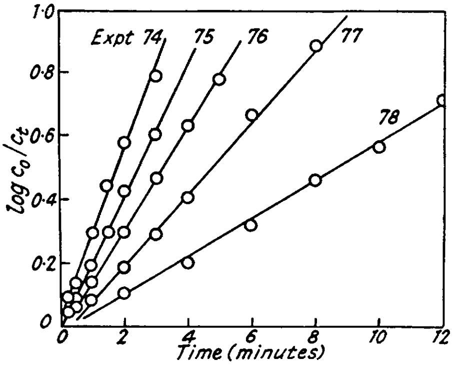


FIG. 4.

Reaction of cobaltic ion with methyl alcohol, showing first-order rate law.



Primary Aliphatic Alcohols.—The reactions of methyl, ethyl, and *n*-propyl alcohol with the cobaltic ion have been examined. The oxidation of methyl alcohol appears to be more complex than those of the other two compounds, which gave similar results and thus are oxidised according to a common mechanism.

Methyl alcohol. The reaction showed a well-defined short induction period which increased with decrease in concentration of methyl alcohol. With considerable excess of methyl alcohol in 5N-sulphuric acid and initial cobaltic-ion concentrations of about $0{\cdot}5 \times 10^{-2}$M. the rate of disappearance of cobaltic ion obeyed a first-order law. These facts are clearly shown in Fig. 4 which gives the first-order plots for the disappearance of cobaltic ion at various methyl alcohol concentrations. This first-order constant was directly proportional to the methyl alcohol concentration. Hence the rate of the reaction after the induction period may be represented by

$$-d[Co^{+++}]/dt = k[Co^{+++}][MeOH]$$

The results of the temperature dependence of the reaction velocity are shown in Fig. 5. It is at once evident from the non-linearity of the plot that k must be a complex quantity containing more than one factor which is temperature dependent.

FIG. 5.

Effect of temperature on the reaction between cobaltic ion and methyl alcohol 5N-*sulphuric acid.*

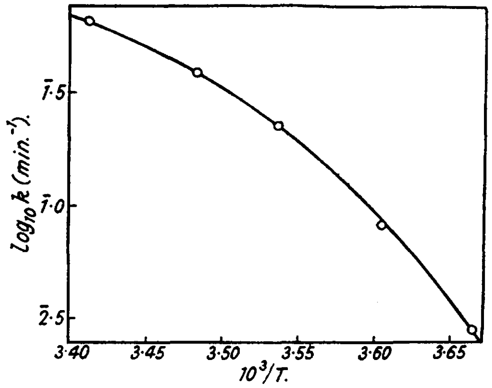
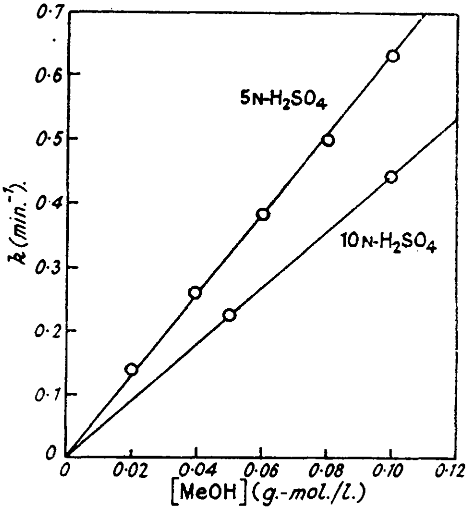


FIG. 6.

Effect of methyl alcohol concentration on the rate of the reaction of cobaltic ion with methyl alcohol in 5N- *and* 10N-*sulphuric acid at* 20·1°.



The results of two experiments at different methyl alcohol concentrations in 10N-sulphuric acid, and the first-order constants so obtained, are included in Fig. 6. It will be seen that an increase in the acid concentration causes a marked decrease in the rate of the reaction.

No gas formation was observed during the reaction, and the product was shown to be largely if not entirely formic acid. Separation of the formic acid by distillation and determination by titration showed that over a five-fold range of alcohol concentration the fraction—moles of acid produced/cobaltic ion consumed—was equal to 1·0, within the experimental error.

FIG. 7.

Effect of ethyl alcohol concentration on the rate of the reaction of cobaltic ion with ethyl alcohol in 5N-*sulphuric acid at* 20·1°.

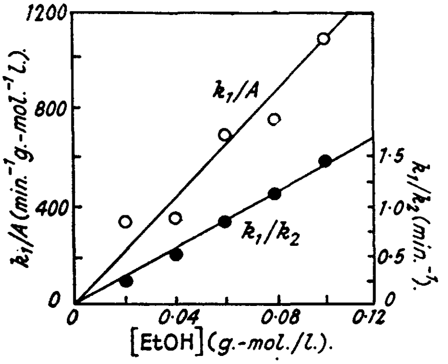
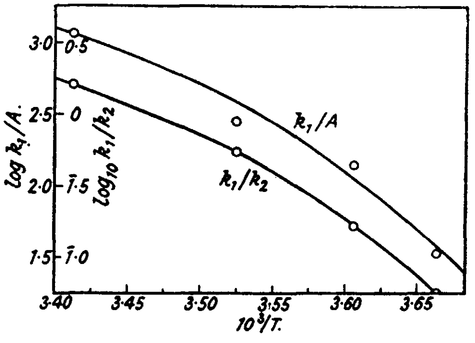


FIG. 8.

Effect of temperature on the reaction between cobaltic ions and ethyl alcohol in 5N-*sulphuric acid.*



Ethyl alcohol. The rate of disappearance of the cobaltic ion in the presence of a large excess of ethyl alcohol in 5N-sulphuric acid was found to be best fitted by a rate equation of the same form as that required for formaldehyde, *viz.*

$$-d[Co^{+++}]/dt = k_1[Co^{+++}]^2/(A + k_2[Co^{+++}])$$

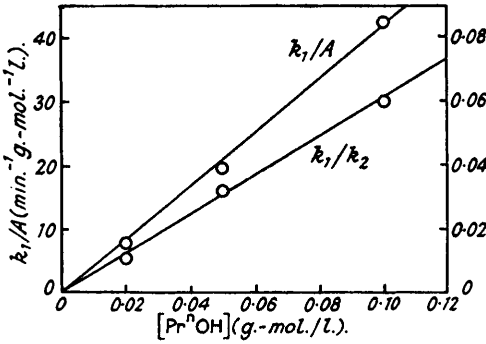
As with formaldehyde, values of k_1/A were obtained from the initial slopes of plots of R/c against c and values of k_1/k_2 were obtained from the initial slopes of first-order plots. The data thus obtained being used, the plots of k_1/A and k_1/k_2 were found to be directly proportional to the ethyl alcohol concentration as is shown in Fig. 7. Thus the rate equation for the loss of cobaltic ion may be expressed as

$$-\mathrm{d}[Co^{+++}]/\mathrm{d}t = k_1[EtOH][Co^{+++}]^2/(A + k_2[Co^{+++}])$$

Runs were carried out at a number of temperatures to examine the temperature dependence of k_1/A and k_1/k_2, and the results obtained are shown in Fig. 8. Curves were obtained in both cases indicating, as was to be expected, different temperature coefficients for each of the constants A, k_1, and k_2.

FIG. 9.

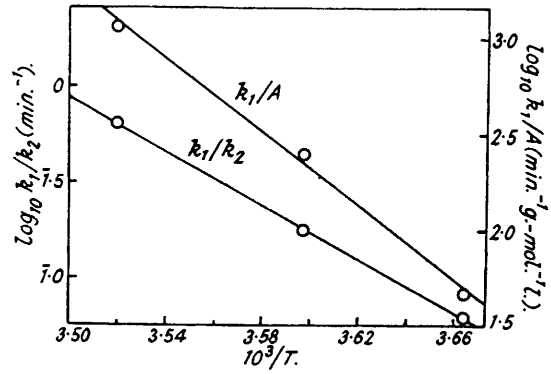
Effect of n-*propyl alcohol concentration on the rate of the reaction between the cobaltic ion and* n-*propyl alcohol in* 5N-*sulphuric acid at* 0°.



n-*Propyl alcohol.* The results obtained with this compound were exactly parallel to those with ethyl alcohol, and obeyed the same rate equation. As before, values of k_1/A and k_1/k_2 were proportional to the *n*-propyl alcohol concentration, as is shown in Fig. 9. In this case, however, plots of $\log_{10} k_1/A$ and $\log_{10} k_1/k_2$ against $1/T$ were found to be linear (Fig. 10).

FIG. 10.

Effect of temperature on the rate of the reaction between n-*propyl alcohol and the cobaltic ion in* 5N-*sulphuric acid.*



DISCUSSION.

Mechanism of Oxidation of Formaldehyde.—The initiation step in the oxidation is the reduction of the cobaltic ion to the cobaltous state and this may be conveniently represented by

$$HCHO + Co^{+++} \longrightarrow CHO\cdot + H^+ + Co^{++}$$

It is highly probable that the cobaltic ion is co-ordinated to water, and the preliminary process leading to decomposition or reaction may be the replacement of one of the co-ordinated molecules of the cobaltic shell by formaldehyde. Although there is no direct evidence for this replacement in this particular case aldehydes are known to form complexes with other heavy-ion salts (Davis and Green, *J. Amer. Chem. Soc.*, **1940**, **62**, 1272). Initial complex formation therefore being assumed, the following reaction mechanism is proposed which is in broad agreement with the experimental findings :

$$\mathrm{HCHO} + \mathrm{Co}^{+++} \longrightarrow (\mathrm{HCHO{\cdot}Co}^{+++}) \tag{1}$$
$$(\mathrm{HCHO{\cdot}Co}^{+++}) \longrightarrow \mathrm{Co}^{++} + \mathrm{H}^{+} + \mathrm{HCO}\cdot \tag{2}$$
$$\mathrm{HCO}\cdot + \mathrm{Co}^{+++} \longrightarrow \mathrm{Co}^{++} + \mathrm{H}^{+} + \mathrm{CO} \tag{3}$$
$$\mathrm{HCO}\cdot + \mathrm{H_2O} \longrightarrow \mathrm{HCHO} + \mathrm{OH}\cdot \tag{4}$$
$$\longrightarrow \mathrm{HCO_2H} + \mathrm{H}\cdot \tag{5}$$
$$\mathrm{OH}\cdot + \mathrm{HCHO} \longrightarrow \mathrm{H_2O} + \mathrm{HCO}\cdot \tag{6}$$
$$\longrightarrow \mathrm{HCO_2H} + \mathrm{H}\cdot \tag{7}$$
$$\mathrm{H}\cdot + \mathrm{H_2CO} \longrightarrow \mathrm{H_2} + \mathrm{HCO}\cdot \tag{8}$$

This scheme gives for the rate of loss of cobaltic ion

$$-\mathrm{d}[\mathrm{Co}^{+++}]/\mathrm{d}t = k_1[\mathrm{HCHO}][\mathrm{Co}^{+++}] + k_3[\mathrm{HCO}\cdot][\mathrm{Co}^{+++}]$$

and by using the usual stationary-state method for intermediates this rate expression becomes

$$-\mathrm{d}[\mathrm{Co}^{+++}]/\mathrm{d}t = k_1[\mathrm{HCHO}][\mathrm{Co}^{+++}] + k_1k_3[\mathrm{Co}^{+++}]^2[\mathrm{HCHO}]/(k_3[\mathrm{Co}^{+++}] + k_5[\mathrm{H_2O}])$$

which is of similar form to that of the experimental relationship. Therefore, the reaction will show a first- or second-order dependence on the cobaltic-ion concentration according as the term $k_3[\mathrm{Co}^{+++}]/k_5[\mathrm{H_2O}]$ is much less than or much more than unity, and this will be determined by the relative rates of reactions (3) and (5).

Mechanism of Oxidation of Alcohols.—Superficially the oxidation of methyl alcohol appears to be considerably simpler than that of the higher alcohols, and the second-order velocity of reaction indicates that the measured process is

$$(1) \quad \mathrm{MeOH} + \mathrm{Co}^{+++} \longrightarrow \mathrm{MeO}\cdot + \mathrm{H}^{+} + \mathrm{Co}^{++} \quad (k_1)$$

which gives as rate equation

$$-\mathrm{d}[\mathrm{Co}^{+++}]/\mathrm{d}t = k_1[\mathrm{Co}^{+++}][\mathrm{MeOH}]$$

However, the presence of the short induction period, the effect of acid concentration on the rate, and the non-linear dependence of $\log_{10} k$ upon $1/T$ militate against the above simple scheme.

The reduction in velocity constant when the acid concentration is raised from 5N- to 10N-sulphuric acid may be a genuine effect of change of medium on the rate, or it may imply that in addition to the reaction of the cobaltic ion with methyl alcohol there is also a reaction with the methoxide ion. The ionic product of methyl alcohol is very small; Hammett (" Physical Organic Chemistry," McGraw Hill, 1940, p. 256) gives the value $K_{\mathrm{MeOH}} = 10^{-16.7}$, and thus at the high acidity used the methoxide-ion concentration would be of the order of 10^{-17}M. If then the reaction between this ion and the cobaltic ion plays any part its rate constant must be very large indeed, compared with that for the methyl alcohol–cobaltic ion reaction. On the other hand, methyl alcohol is a weak proton acceptor and consequently in strongly acid solution it is possible that the reaction

$$\mathrm{MeOH} + \mathrm{OH_3}^{+} \longrightarrow \mathrm{MeOH_2}^{+} + \mathrm{H_2O}$$

may occur and maintain an appreciable proportion of the methyl alcohol in the " methoxonium " state. If this is so and if the " methoxonium " ion, in view of its charge, reacts less readily with the cobaltic ion than does the neutral molecule then this would present an alternative explanation of the decrease in rate when the acid concentration is raised.

The occurrence of these processes introduces the additional reaction (*a*) or (*b*)

$$(a) \quad \mathrm{MeO}^{-} + \mathrm{Co}^{+++} \longrightarrow \mathrm{MeO}\cdot + \mathrm{Co}^{++} \quad (k_2)$$
$$(b) \quad \mathrm{MeOH_2}^{+} + \mathrm{Co}^{+++} \longrightarrow \mathrm{MeO}\cdot + 2\mathrm{H}^{+} + \mathrm{Co}^{++} \quad (k_3)$$

so that

$$-\mathrm{d}[\mathrm{Co}^{+++}]/\mathrm{d}t = k_1[\mathrm{Co}^{+++}][\mathrm{MeOH}] + k_2[\mathrm{Co}^{+++}][\mathrm{MeO}^{-}] \text{ (or } + k_3[\mathrm{Co}^{+++}][\mathrm{MeOH_2}^{+}])$$

making the observed first-order constant, k :

$$\text{either} \quad k = k_1[\mathrm{MeOH}] + k_2[\mathrm{MeO}^{-}]$$
$$\text{or} \quad k = k_1[\mathrm{MeOH}] + k_3[\mathrm{MeOH_2}^{+}]$$

Thus if, as is probable, k_2 or k_3 possessed different temperature coefficients from k_1 then $\log_{10} k$ would not show linear dependence on $1/T$.

As a complete reaction sequence leading to the production of formic acid the following is the simplest which can be envisaged (excluding for the moment any contribution of MeO^- or $MeOH_2^+$)

$$\begin{aligned} MeOH + Co^{+++} &\longrightarrow MeO\cdot + H^+ + Co^{++} \\ MeO\cdot + H_2O &\rightleftharpoons MeOH + OH\cdot \\ MeO\cdot + Co^{+++} &\longrightarrow HCHO + H^+ + Co^{++} \end{aligned}$$

followed by the sequence of reactions given in the previous section for the oxidation of formaldehyde to formic acid. Treatment of this scheme by the stationary-state method leads to a complex rate equation which can with reasonable assumptions be reduced to the simple form found experimentally.

The close similarity of the kinetic results of ethyl and propyl alcohol makes it clear that the mechanisms in the two cases must be essentially the same. As regards the products of oxidation, those of *n*-propyl alcohol have not been studied, but with ethyl alcohol oxidised by a considerable excess of cobaltic sulphate, Swann and Xanthakos (*J. Amer. Chem. Soc.*, 1931, **53**, 400) showed that acetaldehyde and acetic acid were produced together with some 4% of carbon dioxide. It is a reasonable assumption, in view of the similar kinetics, that with *n*-propyl alcohol the products will be only *n*-propaldehyde and *n*-propionic acid.

A relatively simple reaction scheme applicable to either ethyl or *n*-propyl alcohol (by making the appropriate substitutions) which leads to these products is the following :

$$\begin{aligned} C_2H_5\cdot OH + Co^{+++} &\longrightarrow C_2H_5O\cdot + H^+ + Co^{++} \\ C_2H_5O\cdot + H_2O &\rightleftharpoons C_2H_5\cdot OH + OH\cdot \\ C_2H_5O\cdot + Co^{+++} &\longrightarrow CH_3\cdot CHO + H^+ + Co^{++} \end{aligned}$$

followed by a sequence of reactions in which acetaldehyde is oxidised to acetic acid. The latter reaction has not been studied, although it is known from investigation of the trace-metal catalysed oxidation in the presence of molecular oxygen (Bawn and Williamson, unpublished results) that the reaction

$$CH_3\cdot CHO + Co^{+++} \longrightarrow CH_3\cdot CO\cdot + H^+ + Co^{++}$$

is highly probable. Further examination of these reactions is being carried out, and a detailed reaction scheme must await the accumulation of knowledge of the elementary reactions and the stoicheiometry relationships for the overall reaction.

CONCLUSIONS.

From this preliminary survey it is possible to draw a few simple conclusions about the reactions of the cobaltic ion with aldehydes and alcohols. In spite of the varied and complex kinetic features of the reactions it appears that they possess a certain similarity. The primary step in all cases appears to be an electron transfer between the cobaltic ion and the organic compound (or complex with the metal ion) with the generation of a free radical. The radical thus produced may then react with the solvent, the original organic compound, a further radical, or a cobaltic ion, the observed kinetics depending on the relative rates of these processes. It is also apparent that, wherever reaction between cobaltic ion and an ionised form of the organic compound (*e.g.*, formate ion) is possible, this is the preferred initial step, the rates of the reactions with ionised forms being enormously greater than those of neutral molecules.

THE UNIVERSITY, LIVERPOOL.

[*Received, July 25th,* 1950.]