76. *Reactions of the Cobaltic Ion. Part II. The Kinetics of the Reaction of the Cobaltic Ion with Formic Acid.*

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

The oxidation of formic acid by the cobaltic ion in 2—8N-sulphuric acid occurs according to the stoicheiometric equation :

$$2Co^{+++} + HCO_2H \longrightarrow CO_2 + 2Co^{++} + 2H^+$$

The rate-determining process has been shown to be the electron-transfer reactions

$$Co^{+++} + HCO_2H \longrightarrow Co^{++} + HCO_2 + H^+$$
$$Co^{+++} + HCO_2^- \longrightarrow Co^{++} + HCO_2$$

The dependence of the reaction rate on temperature and ionic strength has been measured. The reactions of the formyl radical are discussed.

The oxidation–reduction potential of the cobaltic–cobaltous system is so high (~1·8 v.) that the cobaltic ion should be capable of oxidising a wide variety of organic compounds. The only relevant experiments which have been reported are those of Swann and Xanthakos (*J. Amer. Chem. Soc.*, 1931, **53**, 400), who found that cobaltic sulphate would oxidise pentene, benzene, acetic acid, ethyl alcohol, acetone, and glycerol and would quantitatively oxidise ethylene glycol, formic acid, tartaric acid, citric acid, and malic acid to carbon dioxide. It has also been found recently (Tipper, private communication) that cobaltic sulphate in 5—10N-sulphuric acid reacts readily with acetylene, carbon dioxide being one of the products, whilst the present authors have observed that under similar conditions reaction also occurs with dioxan, sugars, alcohols, and formaldehyde. Cobaltic sulphate in acid media also initiates the polymerisation of vinyl compounds.

Some preliminary kinetic experiments on a few representative organic compounds have therefore been made in order to gain some insight into the general features of the mechanisms of these reactions. These results are reported in the following paper, and the present investigation deals with the oxidation of formic acid which has been studied in greater detail.

As the cobaltic ion decomposes in aqueous solution with the liberation of the hydroxyl radical (preceding paper) it was possible that the reactions with organic compounds would be those of that radical. This view however would appear to be untenable for the following reason. The experiments reported in this and the subsequent paper were carried out in 2·5—10N-sulphuric acid. Under these conditions, with a cobaltic-ion concentration of $\sim 10^{-2}$M., the reaction with water at room temperature is very slow and takes several days to complete, but on addition of the organic compound ($\sim 10^{-1}$M.) the reaction goes to completion in 30—60 minutes. It would therefore appear that the cobaltic ion itself must react directly with the organic compound and not merely serve as a source of hydroxyl radicals.

Experimental.

Materials.—All reagents used were of AnalaR grade. Cobaltic sulphate was prepared by Swann and Xanthakos's method (*J. Amer. Chem. Soc.*, 1931, **53**, 400).

Estimation of Cobaltic Ion.—This was carried out by Noyes and Deahl's method as described in the preceding paper.

Kinetic Measurements.—Rate of reaction of cobaltic ion. Mixtures containing the appropriate concentrations of formic acid, sulphuric acid, and potassium hydrogen sulphate, to give the hydrogen-ion concentration and ionic strength required, were allowed to reach a steady temperature in a vessel immersed in a thermostat. A roughly weighed quantity of cobaltic sulphate was then added, to give an initial cobaltic-ion concentration of ~N/100. Samples were removed at appropriate intervals and analysed for cobaltic ion. Below room temperature a large Dewar vessel containing water cooled with ice was used in place of a thermostat. All experiments were carried out in a large excess of formic acid so that its concentration could be regarded as constant.

The hydrogen-ion concentration in the sulphuric acid–potassium hydrogen sulphate used was calculated on the basis of the two following assumptions :

(*a*) The dissociation $H_2SO_4 \longrightarrow H^+ + HSO_4^-$ was complete, and

(*b*) The dissociation $HSO_4' \longrightarrow H^+ + SO_4^{--}$ could be neglected.

Rate of evolution of carbon dioxide. The apparatus consisted of a conical flask with a ground-glass stopper carrying a short length of capillary tubing. A side arm of approximately 7—8 ml. capacity fitted with small ground-glass stopper was fused on to the vessel. The whole was immersed in a thermostat and vigorously agitated by means of an electrically driven rocking mechanism. The vessel was connected through a length of narrow-bore pressure tubing and a three-way tap to a water manometer (50 cm.). The other limb of the manometer was connected to a large vessel immersed in the thermostat and possessing a tap connecting it to the atmosphere. This vessel effectively served as a constant-pressure source and obviated any effects of changing atmospheric pressure.

The appropriate solution of formic acid, potassium hydrogen sulphate and part of the sulphuric acid was placed in the flask. In the side arm were placed 5 ml. of a solution of cobaltic sulphate in sulphuric acid sufficient to give, when mixed with the bulk of the solution a cobaltic-ion concentration of N/100 and to bring the sulphuric acid concentration to the desired value. The shaker was started immediately after the mixing, and the taps connecting the apparatus with the atmosphere were simultaneously closed. This time was taken as the zero, and the rate was followed by reading the manometer at convenient intervals.

Stoicheiometric Measurements.—The apparatus consisted of the reaction vessel used to investigate the rate of carbon dioxide production connected by pressure tubing and a three-way tap to a gas burette.

As in the kinetic experiments a solution of formic acid, potassium hydrogen sulphate and part of the sulphuric acid was placed in the flask and at the same time a test-tube containing 10—15 ml. of a sulphuric acid solution of cobaltic sulphate of the appropriate concentration was allowed to reach temperature equilibrium in the thermostat. 5 Ml. of the cobaltic solution were removed for cobaltic-ion content determination, and a further 5 ml. of the solution were placed in the side-arm of the reaction vessel, and the tap connecting the system with the atmosphere closed. The gas burette was then read, the contents of side arm and vessel mixed and reaction allowed to proceed to completion with occasional vigorous agitation.

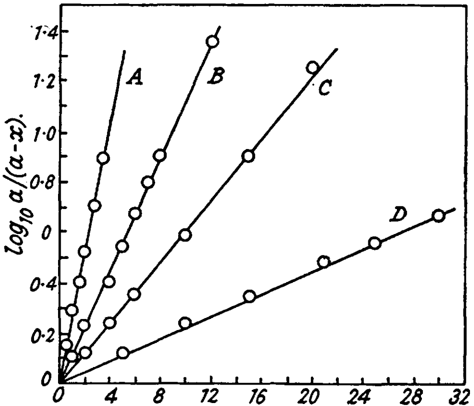
To correct for the volume of carbon dioxide dissolved by the reaction mixture a series of experiments was carried out in which the cobaltic ion in the side-arm was replaced by a standard solution of sodium hydrogen carbonate. Observed and calculated carbon dioxide evolutions were then compared, and from the results correction factors were obtained which could be applied to the stoicheiometric experiments.

RESULTS.

Formic Acid.—In the presence of a large excess of formic acid the rate of disappearance of the cobaltic ion was found to be accurately of first order. Fig. 1 shows a typical group of first-order plots for various formic acid concentrations. The values of the first-order constants thus obtained were also found to be a linear function of the formic acid concentration, as is shown in Fig. 2. The rate equation is thus

FIG. 1.

Oxidation of formic acid by cobaltic ion.

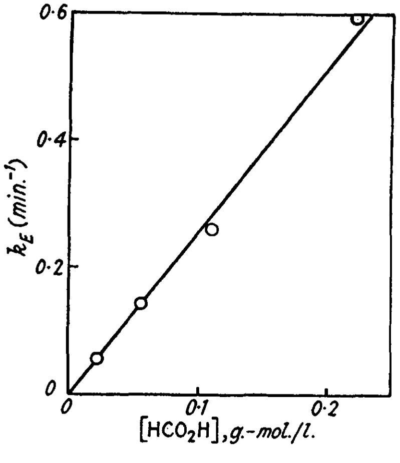


First-order plots for the rate of the reaction of cobaltic ion.

Initial [Co^{+++}] ~ N/200, T = 30·5°; *medium*, 5N-*sulphuric acid.* [HCO$_2$H]: *A*, 0·221; *B*, 0·111; *C*, 0·0553; *D*, 0·0221, *g.-mol./l.*

FIG. 2.

Effect of formic acid concentration on the rate of the reaction of cobaltic ion. T = 30·5°; *medium*, 5N-*sulphuric acid.*



$$-d[\mathrm{Co}^{+++}]/dt = k[\mathrm{HCO_2H}][\mathrm{Co}^{+++}]$$

However, it is also possible that in addition to the undissociated formic acid molecule the formate ion may react with the cobaltic ion, the rate equation in this case being

$$-d[\mathrm{Co}^{+++}]/dt = k_1[\mathrm{HCO_2H}][\mathrm{Co}^{+++}] + k_2[\mathrm{HCO_2}^-][\mathrm{Co}^{+++}]$$

As in the above measurements the formic acid was in large excess, its concentration can be regarded as constant. The hydrogen-ion concentration was also constant, since all the measurements were made in 5N-sulphuric acid, and thus the concentration of formate ion may be regarded as constant;

consequently the reaction would still appear accurately first order with respect to the cobaltic ion. The observed first-order constant k_0 would be given by

$$k_0 = k_1[HCO_2H] + k_2[HCO_2^-]$$

In order to confirm that the formate ion as well as the molecule was a reactive entity a series of runs was carried out at constant ionic strength and formic acid concentration but at a series of different hydrogen-ion concentrations and temperatures. Since $[HCO_2^-] = K[HCO_2H]/[H^+]$, where K is the dissociation constant of formic acid, the above rate equation may now be expressed as

$$-d[Co^{+++}]/dt = \{k_1[HCO_2H] + k_2K[HCO_2H]/[H^+]\}[Co^{+++}]$$

The apparent first-order constant k_E, obtained in the presence of a large excess of formic acid, will be given by the term in the braces and would show a linear dependence on $1/[H^+]$. The values of the first-order constant obtained at temperatures from 0° to 30° are shown plotted against $1/[H^+]$ in Fig. 3. It will be seen that in all cases a linear relationship is obtained, in complete harmony with the above view of the processes contributing to removal of cobaltic ion.

The values of the two rate constants k_1 and k_2 can readily be obtained from the intercepts and slopes, respectively, of the plots shown in Fig. 3, if the value of K under the experimental conditions is known. Direct measurement of K in the medium used (sulphuric acid–potassium hydrogen sulphate solutions) is not practicable. Consequently it was necessary to use values of K reported for other media. Values of K obtained by Kiss and Virmanczy (*Z. physikal. Chem.*, 1934, *A*, **171**, 25) and Larsson and Adele (*ibid.*, 1931, *A*, **156**, 381) at ionic strengths of up to 4 in potassium chloride and sodium chloride have been utilised and values of K at temperatures other than those covered by these measurements were obtained by application of the Harned and Embree (*J. Amer. Chem. Soc.*, 1934, **56**, 1050) relationship between K and temperature.

FIG. 3.

Effect of temperature on the rate of the reaction of cobaltic ion with formic acid (μ = 4·0).

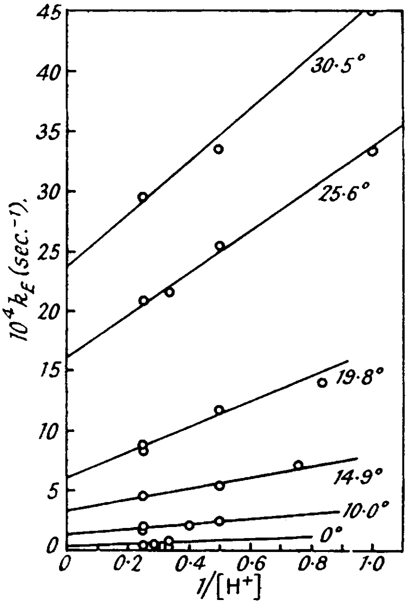
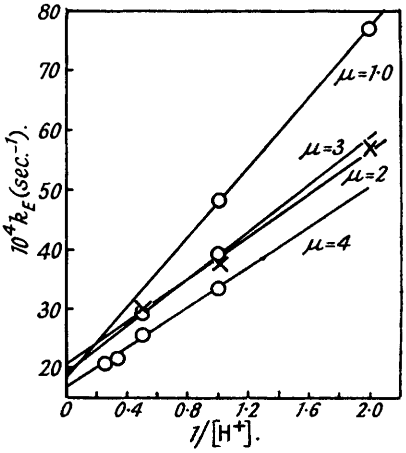


FIG. 4.

Effect of ionic strength. T = 25·6°.



The values of k_1 and k_2 thus obtained at different temperatures are given in Table I.

TABLE I.

k_1 and k_2 in sec.$^{-1}$ g.-mol.$^{-1}$ l.; ionic strength = 4·0.

T, ° K.	303·6	298·7	292·9	288·0	283·1	273·1
10^3k_1	29·7	13·0	4·72	2·14	0·886	0·190
k_2	440	161	99·3	56·0	25·4	6·95

The energies of activation for the two reactions were obtained from the slopes of plots of $\log_{10}k$ against $1/T$, the values obtained being :

$$\text{for } k_1,\ E_1 = 26{\cdot}9 \text{ kcal./mol.}; \quad \text{for } k_2,\ E_2 = 21{\cdot}7 \text{ kcal./mol.}$$

The corresponding frequency factors, A_1 and A_2, calculated from the Arrhenius equation were $A_1 = 6{\cdot}76 \times 10^{17}$ and $A_2 = 1{\cdot}95 \times 10^{18}$, respectively.

The values of the entropy of activation for the reactions were then calculated by means of the statistical mechanical expression for the frequency factor of a bimolecular reaction in solution (Glasstone, Laidler, and Eyring," Theory of Rate Processes," McGraw Hill, 1941):

$$A = \frac{\mathrm{e}kT}{h}\mathrm{e}^{\frac{\Delta S}{R}}$$

The values obtained being: for k_1, $\Delta S_1 = 21{\cdot}1$ cal./°c; for k_2, $\Delta S_2 = 23{\cdot}2$ cal./°c.

The effect of ionic strength on the rate of the reaction is presented in the form of a plot of k_E against $1/[\mathrm{H}^+]$ for various ionic strengths in Fig. 4. The values of k_1 and k_2 derived from these results together with the values of K used in the calculation of k_2 are given in Table II.

TABLE II.

k_1 and k_2 in sec.$^{-1}$ g.-mol.$^{-1}$ l.; $T = 25{\cdot}6°$ c.

μ.	1.	2.	3.	4.
10^3k_1	15·7	16·6	16·8	13·1
10^4K	2·92	2·05	1·33	0·846
k_2	78·5	71·6	97·1	162

These results do not obey the Brønsted relationship because of the high values of μ, although the effect of μ on k_1 is much smaller than that on k_2, as would be expected from the fact that k_1 refers to an ion–molecule and k_2 an ion–ion reaction.

Results obtained by measurement of the rate of carbon dioxide production are given in Table III. The column k_{CO_2} gives the experimentally determined first-order constant for the rate of evolution of carbon dioxide, whereas the column k_E gives, for comparison, the observed first-order constants for the rate of disappearance of cobaltic ion under identical conditions.

TABLE III.

Initial $[\mathrm{Co}^{+++}] = \mathrm{N}/200$; $\mu = 4{\cdot}0$.

T, ° c.	$[\mathrm{HCO_2H}]$, N.	$[\mathrm{H}^+]$, N.	$10^4k_{\mathrm{CO}_2}$ (sec.$^{-1}$).	10^4k_E (sec.$^{-1}$).
25·1	0·125	4·0	19·1	19·0
25·1	0·125	2·0	22·9	23·2
25·1	0·219	4·0	33·6	33·4
30·3	0·125	4·0	41·9	47·8

It will be seen that within the limits of experimental error k_{CO_2} and k_E are the same, under identical conditions.

Finally, the results of measurements of the stoicheiometric ratio of carbon dioxide produced to cobaltic ion consumed are given in Table IV.

TABLE IV.

$T = 29°$ c.; $[\mathrm{H}^+] = 4$N.; $\mu = 2{\cdot}0$.

$[\mathrm{HCO_2H}]$, N.	Ml. $\mathrm{KMnO_4} \equiv$ 5 ml. Co^{+++}.	$\frac{+\Delta\mathrm{CO_2}}{-\Delta\mathrm{Co}^{+++}}$.	$[\mathrm{HCO_2H}]$, N.	Ml. $\mathrm{KMnO_4} \equiv$ 5 ml. Co^{+++}.	$\frac{+\Delta\mathrm{CO_2}}{-\Delta\mathrm{Co}^{+++}}$.
0·0625	5·18	0·521	0·0625	6·10	0·525
0·0625	4·66	0·502	0·0625	7·08	0·516
0·0625	4·99	0·496	0·25	6·88	0·511
0·0625	4·96	0·488	0·25	9·16	0·525
0·0625	4·72	0·522			

Variation of either $[\mathrm{HCO_2H}]$ or $[\mathrm{Co}^{+++}]$ does not affect this ratio, the value of which may be taken to be 0·5 within the limits of experimental error.

DISCUSSION.

The oxidation of formic acid by cobaltic ion was shown by Swan and Xanthakos to lead to a 100% yield of carbon dioxide. Thus any postulated reaction mechanism should not only account for this product but also yield correct kinetics and explain the stoicheiometric relationships observed. The following sequence of reactions satisfactorily accounts for these facts.

$$\mathrm{HCO_2H} + \mathrm{Co}^{+++} \longrightarrow \mathrm{HCO_2}\cdot + \mathrm{H}^+ + \mathrm{Co}^{++} \quad . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{HCO_2}^- + \mathrm{Co}^{+++} \longrightarrow \mathrm{HCO_2}\cdot + \mathrm{Co}^{++} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{HCO_2H} \rightleftharpoons \mathrm{HCO_2}^- + \mathrm{H}^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{HCO_2}\cdot + \mathrm{H_2O} \rightleftharpoons \mathrm{HCO_2H} + \mathrm{OH}\cdot \quad . \; . \; . \; . \; . \quad (4) \text{ and } (5)$$

$$\mathrm{OH}\cdot + \mathrm{HCO_2}\cdot \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$\mathrm{HCO_2}\cdot + \mathrm{HCO_2}\cdot \longrightarrow \mathrm{HCO_2H} + \mathrm{CO_2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$\mathrm{HCO_2}\cdot + \mathrm{Co}^{+++} \longrightarrow \mathrm{Co}^{++} + \mathrm{H}^+ + \mathrm{CO_2} \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

Primary electron-transfer processes of the type (1) and (2) are necessary to explain the observed kinetics and are also in harmony with investigations on the reactions of cobaltic ions with water and other organic molecules. The exact fate of the formyl radical thus formed is, however, much less certain. The possible secondary-reaction schemes (4), (5), and (6), or (7), conform to the experimental findings, each leading to the experimental stoicheiometric fraction for CO_2/Co^{+++} of 0·5 and also to the observed rate equation. The occurrence of reaction (5) has already been postulated by Weiss (*J. Phys. Chem.*, **1937**, **41**, 1107) to explain the oxidation of formic acid by hydrogen peroxide. Although reaction (4) may require a small activation energy it should occur readily at room temperature. Reactions (6) and (7), involving the transfer of a hydrogen atom between a pair of radicals, would be equally probable and require little or no activation.

An unequivocal decision between these alternative secondary reactions is thus not possible but the former is more likely since, owing to the overwhelming concentration effect of the water, the formyl radical would be preferentially consumed by reaction (4) rather than (7).

Reaction (8) which is also a possible source of carbon dioxide may be excluded since its occurrence would lead to a kinetic dependence of the cobaltic-ion concentration different from that observed.

It is not our intention to discuss the theoretical aspects of the elementary processes in this paper but it is noteworthy that the activation energy of the reaction of the cobaltic ion with the formate ion is 5·2 kcal. less than with the formic acid molecule. This is understandable as in the former case the electrostatic energy of interaction is available to bring the reactants together.

The similar magnitudes of the entropies of activation indicate, as was to be expected, that the activated complex in the two cases must be closely similar. The entropy factor for the ion–ion reaction is larger than for the ion–molecule reaction, and this is understandable as there must be a greater change in solvation on the formation of the activated complex, of charge 2^+, in the first case than in the second where the charge remains at 3^+.

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THE UNIVERSITY, LIVERPOOL. [*Received, July 25th,* 1950.]