

### 389. *Reactions of the Cobaltic Ion. Part VII.\* The Stability and Reactivity of Cobaltic Acetate.*

By J. A. SHARP.

Cobaltic acetate in aqueous solution is rapidly reduced to the cobaltous state by the addition of dilute mineral acids. The kinetics of this process have been studied and it is concluded that the primary process is a change of the anions surrounding the cobaltic ion. Some additional properties of cobaltic acetate are summarised.

THE very powerful oxidising action of the cobalt ion towards a wide variety of organic compounds such as olefins, alcohols, aldehydes, and acids has already been reported.<sup>1</sup> In this work the readily isolable cobaltic sulphate which forms stable solutions in acids has been employed, and in spite of the complex features of these reactions the broad general principles of the reactivity emerged in that the primary process was an electron transfer between the cobaltic ion and the organic molecules with the formation of a free radical.

In view of the difficulties of handling cobaltic sulphate and of preparing it free from mineral acid it is preferable in kinetic studies to employ the more stable cobaltic acetate. Little is known about this substance, so a preliminary study of its preparation and properties was carried out.<sup>2</sup> In the present work the stability of aqueous solutions has been investigated and the kinetics of its decomposition in mineral acid measured.

*Properties of Cobaltic Acetate.*—Cobaltic acetate prepared by electrolytic oxidation and purified as already described<sup>2</sup> is stable at room temperature but decomposes at 100° with the evolution of acetic acid. It forms stable solutions in acetic acid and ethyl alcohol and the oxidising power of these solutions remains constant for several months at normal temperatures. The solutions, when heated to 70°, decompose into acetic acid and cobaltous acetate. In aqueous solution the acetate hydrolyses slowly to gelatinous cobaltic hydroxide, and thus behaves differently from other simple cobaltic salts which rapidly decompose in water. Dilute sodium hydroxide or carbonate precipitated cobaltic hydroxide but in dilute mineral acids the cobaltic acetate was reduced to the cobaltous state within a few minutes. The factors which determine this reduction have been investigated and will be described later.

As shown by Sharp and White<sup>2</sup> the absorption spectra of solutions at 2000—10,000 Å

\* Part VI, preceding paper.

<sup>1</sup> Bawn and White, *J.*, 1951, 331, 339, 343; Bawn and Sharp, *J.*, 1957, 1854; Hargreaves and Sutcliffe, *Trans. Faraday Soc.*, 1955, 51, 786.

<sup>2</sup> Sharp and White, *J.*, 1952, 110.

were similar for acetic acid, alcohol, and water as solvents. The presence of a small amount of cobaltous acetate in the cobaltic salt had a negligible effect on the spectra as its maximum molar extinction coefficient (at 5100 Å) was 0.02 of that of cobaltic acetate and the absorption decreased markedly on both sides of the 5100 Å peak. Measurements in these solvents over the wide concentration range  $3.0 \times 10^{-5}$ — $1.5 \times 10^{-2}$ M showed that the absorption at any wavelength was directly proportional to the concentration of the cobaltic acetate in solution. This method, supplemented by other analytical procedures, was used to follow the change in cobaltic concentration in the kinetic studies reported below. Dr. Sutcliffe in this laboratory has shown that the absorption spectra of solutions of cobaltic acetate are similar to that of cobaltic sulphate and cobaltic perchlorate, indicating that the acetate is a simple cobaltic salt  $\text{Co}(\text{OAc})_3$  rather than a hexacoordinated complex  $\text{H}_3\text{Co}(\text{OAc})_6$ . The visible maximum in absorption is at 5000 Å and the ultraviolet absorption is not as intense. In the visible region the steep increase in absorption corresponding to the electron-transfer spectrum starts at a higher wavelength with the acetate than with either the sulphate or perchlorate. In glacial acetic acid the spectrum is more intense than in water, which is in agreement with the view that the salt is ionised in water. Sharp and White<sup>2</sup> showed by conductivity measurements that cobaltic acetate was appreciably ionised in water whereas in glacial acetic acid the equivalent conductivity, which was independent of the age of the solution, was  $3.93 \times 10^{-3}$  mhos (mole/l.)<sup>-1</sup> for a solution of 0.00724N-cobaltic acetate. At this concentration the degree of ionisation is thus  $4.3 \times 10^{-3}$ .

The spectrum of the cobaltic salt formed in dilute aqueous acetic acid by the oxidation of cobaltous acetate with ozone has recently been measured by Hill.<sup>3</sup> The spectrum is of the same type as that obtained with cobaltic acetate but the positions of the maxima obtained by Hill are displaced about 300 Å towards the ultraviolet. Hill suggests that the absorbing species was the  $\text{Co}(\text{OAc})^{2+}$  ion but no real evidence is given to substantiate this view.

*The Stability of Aqueous Solutions of Cobaltic Acetate.*—As already stated the addition of dilute sulphuric acid to an aqueous solution of cobaltic acetate causes complete reduction to the cobaltous state. The rate of this reaction was measured over a range of acid concentrations by following the decrease in concentration of cobaltic ion with a Unicam

TABLE 1. *Second-order decomposition of cobaltic acetate measured with Unicam spectrophotometer at 300 mμ. Temp. = 17°.*

[H <sup>+</sup> ]	10 <sup>3</sup> [Co <sup>3+</sup> ] <sub>initial</sub>	10k̄ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	10 <sup>4</sup> k̄[Co <sup>3+</sup> ] <sub>initial</sub> [H <sup>+</sup> ]
0.6	2.29	4.00	15.3
0.6	1.53	7.83	20.0
0.6	0.76	14.0	17.8
1.2	0.76	26.5	16.9
1.8	0.76	33.0	14.0
0.9	0.76	20.3	17.2
1.2	1.53	13.7	17.3
Measured with Spekker spectrometer with orange filter. Temp. = 18°.			
0.385	0.541	14.50	21.0
0.154	0.72	4.22	19.7
0.77	3.56	4.40	20.4
1.54	2.12	13.00	17.9
1.54	1.22	26.00	20.6

TABLE 2. [Co<sup>3+</sup>]<sub>initial</sub> =  $2.9 \times 10^{-3}$  M. Temp. = 20°. [H<sup>+</sup>] = 0.30.

Me·CO <sub>2</sub> H (M)	10k̄ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	D <sub>2</sub>
0.0	3.10	0.827
0.024	3.24	0.932
0.073	3.95	0.911
0.121	4.35	0.955
0.243	6.00	0.895
0.486	6.35	0.826
0.729	6.57	0.766
2.43	4.71	0.646
4.86	3.10	0.613
12.15	2.06	0.557

spectrophotometer as described in Part IV.<sup>4</sup> The decrease in absorption was rapid over the first few minutes and this was followed by a slower decrease at a rate which was of the

<sup>3</sup> Hill, *J. Amer. Chem. Soc.*, 1949, **71**, 2434.

<sup>4</sup> Bawn and Sharp, *J.*, 1957, 1854.

second order with respect to the change in optical density. Typical data showing the plot of the reciprocal of the optical density with time at several acid concentrations are shown in Fig. 1. Investigation of the factors determining the initial decrease showed that it was greater with high sulphuric acid concentration (Table 1);  $k = d(1/[Co^{3+}])/dt$ . It was also greater for larger concentrations of acetic acid added to the dilute sulphuric

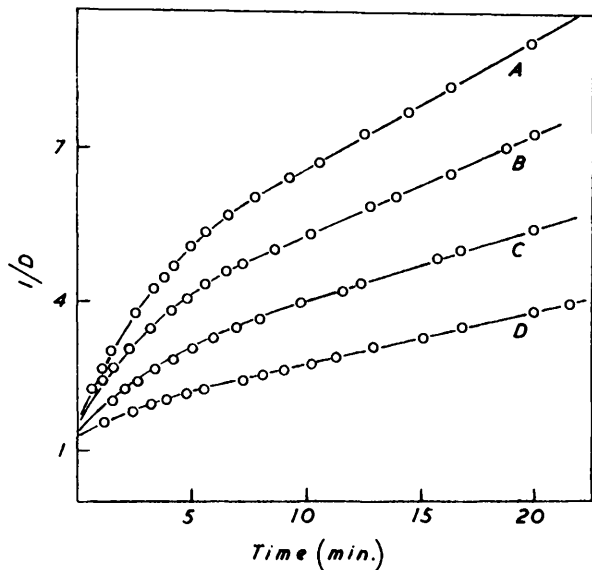
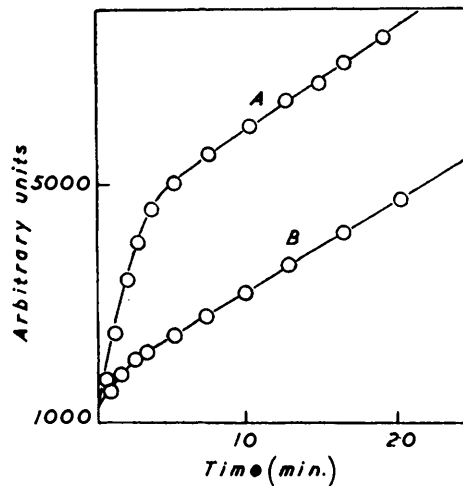


FIG. 1. Rate of alteration of optical density  $D$  at 3000 Å (10 cm. cell).

$[Co^{3+}]_{initial} = 0.76 \times 10^{-4}M$ . Hydrogen-ion concn.: A 1.8, B 1.2, C 0.9, D 0.6M.

FIG. 2. Plots of reciprocals of (A) optical density and (B) concentration against time.



acid solution in which the cobaltic acetate was originally dissolved as shown in Table 2 ( $D_2$  is the ratio of the optical density at the onset of the second-order rate to the initial optical density). The changes can be understood if the initial rapid decrease in absorption is associated with a change in the anions surrounding the cobaltic ion rather than the reduction to the cobaltous state, since cobaltic sulphate is known to have a lower absorption intensity than cobaltic acetate<sup>3</sup> and if a solution of cobaltic acetate in water has a lower absorption than a solution in acetic acid. If this suggestion is correct then the decrease in absorption with time will not parallel the change in oxidising power with time for the

same reaction. With a readily oxidisable substrate such as ferrous iron which is equally rapidly oxidised by cobaltic sulphate, acetate, or intermediate species the latter reaction will measure only the reduction of cobaltic to cobaltous independently of any change in optical absorption. These changes were investigated by observing the decrease in absorption of the solution and simultaneously the decrease in oxidising power by running small samples of the solution into excess of standard ferrous ammonium sulphate solution at fixed intervals and estimating the ferrous ion consumed by back titration with permanganate. Typical plots for a single reaction are shown in Fig. 2. The results confirm the view that the initial rapid decrease in absorption is not associated with a decomposition but with a modification of the co-ordination shell of the ion. The slower stage of the reaction obeys a second-order relation for both the decrease in oxidising power and the decrease in absorption (Fig. 2).

A study of the factor affecting the second stage of the reaction showed (a) that all rates were proportional to the square of the cobaltic concentration (Fig. 1); (b) that the rates were inversely proportional to the total cobalt ion concentration, which is equivalent to the initial cobaltic concentration (Table 1) [this surprising result in conjunction with (a) appears to indicate an overall first-order relationship; this order was not obeyed and all results conformed to the second-power law in cobaltic concentration]; (c) that the second-order rates were directly proportional to the hydrogen-ion concentration (Table 1); (d) that the effect of the addition of increasing amounts of acetic acid to the solution in sulphuric acid, the pH being kept constant, showed an initial increase in rate of reduction followed by a decrease in rate at higher acetic acid concentration (Table 2). The kinetic results in sulphuric acid may be summarised by the relation  $-d[\text{Co}^{3+}]/dt = k[\text{Co}^{3+}]^2[\text{H}^+]/[\text{Co}^{3+}]_{\text{initial}}$ , where  $k = 1.7 \times 10^{-3}$  l. mole<sup>-1</sup> sec.<sup>-1</sup> at 17°. In the presence of acetic acid the rate law contains an additional multiplication term  $[\text{AcOH}]^x$  where  $x$  depends on the acetic acid concentration. Although it is not yet possible to formulate a complete mechanism which accounts for the observed rate law the general picture of the reaction which has emerged is that the addition of sulphuric acid to the cobaltic acetate solution causes a rapid exchange of the anions bound to the cobalt ion. The newly formed cobaltic complex is much less stable than the acetate and the square term in  $[\text{Co}^{3+}]$  indicates that reduction to  $\text{Co}^{2+}$  occurs by interaction of two  $\text{Co}^{3+}$  complexes. A similar term in the rate expression is observed in the cobaltic ion reaction with water<sup>1</sup> and in the decomposition of tetralin hydroperoxide by cobaltic salts.<sup>5</sup>

The author thanks Professor C. E. H. Bawn for his interest and advice.

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,  
THE UNIVERSITY, LIVERPOOL.

[Received, October 12th, 1956.]

<sup>5</sup> Woodward and Mesrobian, *J. Amer. Chem. Soc.*, 1953, **75**, 6189.