BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2246—2247 (1973)

Kinetics of the Formation of Hydrogen Peroxide Induced by the Decomposition of the Trioxalatocobaltate(III) in the Presence of Manganese(II) and of Oxygen

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(Received January 24, 1973)

It has been recently reported[1] that a considerable amount of hydrogen peroxide is formed upon the decomposition of the trioxalatocobaltate(III) complex in an oxygen atmosphere in an acidic solution, and that the amounts of hydrogen peroxide formed increase markedly upon the addition of manganese(II) sulfate. However, no detailed investigation of the kinetics of the reaction has been made yet. In the present paper, the kinetics of the formation of hydrogen peroxide according to the decomposition of the trioxalatocobaltate(III) are investigated in the presence of manganese(II) and in an oxygen-saturated solution.

Experimental

The potassium trioxalatocobaltate(III) was the same as that used in a previous study.[2] The oxalic acid and manganese(II) sulfate were of a guaranteed reagent grade. Pure oxygen gas was bubbled through the reaction mixture. All the experiments were carried out in the dark at 40 °C. The concentration of hydrogen peroxide was determined iodometrically in 0.3 M potassium oxalate in the presence of about 0.01 M molybdate as a catalyst.[3] The iodine thus formed was titrated amperometrically using a rotating platinum electrode. Blank experiments with mixtures of hydrogen peroxide and trioxalatocobaltate(III) solutions of the same compositions as the reaction mixture showed that the method of analysis yielded reliable results. The concentration of trioxalatocobaltate(III) was determined by means of the absorption spectra at 600 nm.

Results and Discussion

TABLE 1. HYDROGEN PEROXIDE FORMATION INDUCED UPON DECOMPOSITION OF TRIOXALATOCOBALTATE(III) IN THE OXYGEN SATURATED SOLUTION AT 40°C IN THE DARK[a]

Time of standing, min	M in $MnSO_4$,			
	0	0.001	0.01	0.1
	$[H_2O_2]_{formed} \times 10^3$, M			
15	0.1	0.45	0.8	0.9
30	0.2	0.94	1.8	2.8
45	0.3	1.3	2.6	4.3
60	0.3	1.7	3.4	5.6
90	0.5	2.3	4.6	7.9
120	0.6	2.9	5.7	9.7
180	0.9	3.8	7.7	13.0
240	1.1	4.4	8.9	
300	1.2	5.1	9.9	

a) Initial solutions of 4.0×10^{-3} M in potassium trioxalatocobaltate(III), 0.01 M in oxalic acid, 0.1 M in sulfuric acid, and the varied concentrations of manganese(II) sulfate.

Table 1 shows results obtained with various concentrations of manganese(II). The rate of the decomposition of trioxalatocobaltate(III) was also measured simultaneously under the same conditions. In all instances, the concentration of trioxalatocobaltate(III) decreased in accordance with the first-order expression of $-d[Co(C_2O_4)_3{}^{3-}]/dt=k[Co(C_2O_4)_3{}^{3-}]$. The decomposition rate decreased slightly upon the addition of manganese(II) sulfate. The values of the rate constant (k) under the condition of Table 1 were 8.2, 7.8, 7.6, and $5.6\times10^{-5}\ \mathrm{sec}^{-1}$ in manganese(II) sulfate of 0, 0.001, 0.01, and 0.1 M respectively. It has been reported previously[2] that k can be described as $k=k_1+k_2[H^+]$. Therefore, the decrease in the reaction rate with an increase in the amount of manganese(II) sulfate may be due to the decrease in the hydrogen-ion concentration with the increase in the amount of the sulfate ion. In the presence of manganese(II), the amount of hydrogen peroxide formed was many times greater than that of the trioxalatocobaltate(III) decomposed. Therefore, a chain reaction must occur in the presence of manganese(II). The initiation reaction is probably the intra-molecule redox reaction of the trioxalatocobaltate(III) complex.[2]

$$Co(C_2O_4)_3{}^{3-} \longrightarrow Co^{II} + 2C_2O_4{}^{2-} + CO_2 + CO_2{}^- \quad (1)$$

$$Co(C_2O_4)_3{}^{3-} + H^+ \longrightarrow Co^{II} + 2C_2O_4{}^{2-} + H^+ + CO_2 + CO_2{}^- \quad (2)$$

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[1] I. M. Kolthoff, E. J. Meehan, and M. Kimura, *J. Phys. Chem.*, **75**, 3343 (1971).

[2] M. Kimura and T. Sato, This Bulletin, **46**, 471 (1973).

[3] I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience, New York, N.Y. (1957), p. 283.

The sequence which follows is analogous to that proposed by Kolthoff *et al.*[1]

$$CO_2^- + O_2 \rightleftarrows O_2CO_2^- \qquad (3)$$

$$O_2CO_2^- + Mn^{II}Ox + 2H^+ \longrightarrow H_2O_2 + Mn^{III}Ox + CO_2 \qquad (4)$$

$$Mn^{III}Ox \longrightarrow Mn^{II}Ox + CO_2 + CO_2^- \qquad (5)$$

The sequence of Reactions (3), (4), and (5) constitutes a chain reaction. The terminating reaction probably occurs *via* Eq. (6):

$$Mn^{III}Ox + CO_2^- \longrightarrow Mn^{II}Ox + CO_2 \qquad (6)$$

where $Mn^{II}Ox$ and $Mn^{III}Ox$ indicate the various forms of oxalato-manganese(II) and (III) respectively. The assumption of steady-state concentrations of CO_2^-, $O_2CO_2^-$, and $Mn^{III}Ox$ leads to Eq. (7):

$$[H_2O_2]_{\text{formed}} = \sqrt{\frac{kk_4k_5K[O_2][Mn^{II}Ox][Co(C_2O_4)_3{}^{3-}]}{2k_6}}[H^+]\tau \qquad (7)$$

where $k=k_1+k_2[H^+]$, where k_n indicates the rate constant of the reaction (n), where K is the equilibrium constant of Reaction (3), and where τ means the time of standing of the reaction mixtures. It may be presumed that the concentrations, $[O_2]$, $[H^+]$, and $[Mn^{II}Ox]$ are constant under the conditions of Tables 1 and 2. Under these circumstances Eq. (7) predicts a linear relation in the plot of $[H_2O_2]_{\text{formed}}/[Co(C_2O_4)_3{}^{3-}]^{1/2}$ *vs.* τ. This is verified experimentally in Fig. 1. The above reaction mechanisms are properly borne out by the fitness of the kinetic treatment. Since the concentration of oxalate does not appear in Eq. (7), the amount of hydrogen peroxide formed must be essentially independent of the concentration of the uncomplexed oxalate ion. However, the following facts should be noted. Manganese(III) as well as manganese(II) forms various complexes with oxalate, and the redox decomposition of Mn(III)Ox occurs at different rates (k_5);[4,5] In acidic solutions under conditions such as are shown in Tables 1 and 2, mono- and di-oxalato complexes of manganese(III) would be presumably predominant species, and the oxalato complexes of manganese(II) may be highly dissociated. The equilibria should be shifted by any change in the concentrations of oxalate and manganese(II) sulfate. Accordingly, the formation of hydrogen peroxide would be dependent on the oxalate concentration. As may be seen in Table 2, a small dependence of the oxalate concentration was observed. However, the amount of hydrogen peroxide formed at 0.5 hr was practically independent of the concentration of oxalic acid. Finally, formic acid was compared with oxalic acid in respect of the hydrogen peroxide formation. As can be seen in Table 2, the amount of hydrogen peroxide formed does not increase when formic acid is added instead of oxalic acid; rather, it decreases slightly. It appears that the following reactions, (4′) and (5′) hardly occur under these conditions:

$$O_2CO_2^- + Mn^{II} + 2H^+ \longrightarrow H_2O_2 + Mn^{III}(\text{formate}) + CO_2 \qquad (4')$$

$$Mn^{III}(\text{formate}) \longrightarrow Mn^{II} + CO_2^- + H^+ \qquad (5')$$

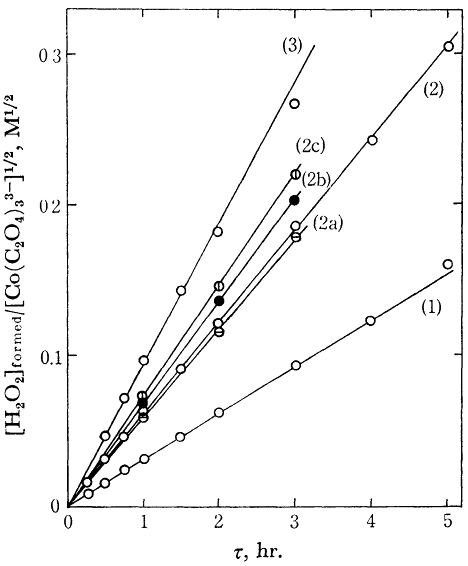

Fig. 1. Plot of $[H_2O_2]_{\text{formed}}/[Co(C_2O_4)_3{}^{3-}]^{1/2}$ *vs.* τ.
Conditions as in Table 1. Concentrations of manganese(II) sulfate are 0.001M (1), 0.01M (2), and 0.1M (3). (2a), (2b), and (2c) are as in (2) except 0.005M, 0.05M, and 0.1M in oxalic acid respectively, instead of 0.01M oxalic acid.

TABLE 2. EFFECT OF THE OXALIC ACID CONCENTRATION ON THE FORMATION OF HYDROGEN PEROXIDE[a)]

$[H_2C_2O_4]_{\text{added}}$, M[b)]	$[H_2O_2]_{\text{formend}} \times 10^3$, M Time of standing, hr			
	0.5	1	2	3
0	1.3	2.5	4.4	6.1
0.005	1.7	3.2	5.4	7.3
0.01	1.8	3.4	5.7	7.7
0.05	1.8	3.8	7.2	9.6
0.1	1.8	4.2	7.6	10.4
0.1 M HCOOH instead of $H_2C_2O_4$	1.1	2.2	3.9	5.2

a) Conditions as in Table 1 except for the varied concentrations of oxalic acid and the 0.01 M value of manganese(II) sulfate.

b) The concentrations of oxalic acid listed here indicate those in the initial solutions.

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[4] a) H. Taube, *J. Amer. Chem. Soc.*, **69**, 4118 (1947); b) H. Taube, *ibid.*, **70**, 1216 (1948).

[5] S. J. Adler and R. M. Noyes, *ibid.*, **71**, 2036 (1955).