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Kinetics of Reduction of Mercury(II) Chloride to Mercury(I) Chloride Induced by the Decomposition of Trioxalatocobaltate(III) in Acid Aqueous Solutions

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Synopsis. The decomposition reaction of trioxalatocobaltate(III) complex in the presence of mercury(II) chloride in acid medium induces the reduction of the latter to mercury(I) chloride (calomel). The results are accounted for by a sequence of a chain reaction which is initiated by the intramolecular redox decomposition of trioxalatocobaltate(III). The formation rate of mercury(I) chloride is expressed as half order with respect to the concentrations of oxalic acid, mercury(II) chloride, and trioxalatocobaltate(III). Mechanisms and kinetics are presented to account for these facts.

The light-initiated reduction of mercury (II) chloride by oxalate in a neutral medium has long been known as Eder's reaction after its discovery.[1] The photochemical reactions of this reaction have been studied by many investigators. Recently, Kimura *et al.*[2] have reported that the slow addition of a trace of a strong oxidizing agent to dilute oxalic acid solutions in dilute sulfuric acid causes the formation of free radicals which can bring about the reduction of mercury (II) chloride to mercury (I) chloride, and also reported briefly that a similar reaction occurs upon the thermal decomposition of trioxalatocobaltate (III) complex in an acid medium. In the present paper, the kinetics of the reduction of mercury (II) chloride to mercury (I) chloride according to the decomposition reaction of trioxalatocobaltate (III) is studied in the acid aqueous solutions.

Experimental

The potassium trioxalatocobaltate(III) was prepared following the directions of Sörensen.[3] All chemicals were of the guaranteed reagent grade. Pure nitrogen gas was bubbled through the reaction mixture. All experiments were carried out in the dark at a given temperature. The amount of mercury(I) chloride formed was determined by weighing after filtering through a glass-sintered crucible, washing, and drying at 80 °C. In order to compare conveniently the amount of mercury(I) chloride with the concentrations of the other species such as oxalic acid, mercury(II) chloride, and so forth, the amount of mercury(I) chloride formed is expressed as molarity which refers to the volume of the reaction mixture. After removal of mercury(I) chloride by filtration, concentrations of trioxalatocobaltate(III) in the filtrates were determined by means of the absorption spectra at 600 nm.

Results and Discussion

The relative efficiency of trioxalatocobaltate (III) in initiating the reaction increases with increasing concentrations of oxalic acid and mercury (II) chloride. Table 1 illustrates this effect over the range 0—0.4 M in oxalic acid, in 0.1 and 0.2 M in mercury (II) chloride at varying the reaction time. The concentration of trioxalatocobaltate (III) decreases in accordance with the first order expression, $-d[Co(C_2O_4)_3^{3-}]/dt=k_0[Co(C_2O_4)_3^{3-}]$ which is the same as that reported in the previous paper.[4] Concentrations of trioxalatocobaltate (III) decomposed are also listed in Table 1. The temperature effect on the formation of mercury (I) chloride was investigated in an initial composition of 0.1 M in oxalic acid, 0.1 M in mercury (II) chloride, and 10^{-3} M in potassium trioxalatocobaltate (III). The data obtained at various temperatures are listed in Table 2. Similarly as in Table 1, the concentrations of trioxalatocobaltate (III) decomposed were determined. But the data are omitted in Table 2. In all the instances, the amount of mercury (I) chloride formed was many times greater than that of trioxalatocobaltate (III) decomposed.

TABLE 1. FORMATION OF MERCURY(I) CHLORIDE INDUCED UPON DECOMPOSITION OF TRIOXALATOCOBALTATE(III)[a]

Oxalic acid M (added)	Reaction time in hr									
	0.5	1	2	3	4	0.5	1	2	3	4
	$[Hg_2Cl_2]_{formed}\times10^3$, M					$[Co(C_2O_4)_3^{3-}]_{decomposed}\times10^4$, M				
0		0.25	0.7	0.82			3.6	5.8	7.2	
0.01		2.6	4.2	4.6	5.8		3.4	5.5	7.2	7.7
0.1	5.2	8.5	12.1	16.0	16.5	1.4	2.4	4.2	6.4	7.4
0.1[b]	8.9	13.0	21	25	29	1.0	2.7	4.9	6.6	7.2
0.2		10.3					2.4			
0.4		11.2					2.4			

a) Initial solutions 1.0×10^{-3} M in potassium trioxalatocobaltate(III), 0.1 M in mercury(II) chloride, 0.1 M in sulfuric acid, and the varied concentrations of oxalic acid. Solution saturated with nitrogen gas; Dark; 40 °C. b) As in a) except 0.2 M in mercury(II) chloride.

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Table 2. Temperature dependence on the formation of mercury(I) chloride[a)]

Temp., °C	Reaction time, hr			
	1	2	3	4
	$[Hg_2Cl_2]_{formed} \times 10^3$, M			
25	0.74	2.3	3.4	
30	2.1	4.7	4.9	7.9
35	4.6	7.5	10.3	12.0
40	8.5	12.1	16.0	16.5

a) Initial solutions 1.0×10^{-3}M in potassium trioxalatocobaltate(III), 0.1 M in oxalic acid, 0.1 M in mercury (II) chloride, and 0.1 M in sulfuric acid; The other conditions are the same as in Table 1.

Therefore, a chain reaction must occur. The initiation reaction is probably the intra-molecular redox decomposition of trioxalatocobaltate (III).[4)]

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

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

The radical which is formed in the above reactions may be either $CO_2^{\cdot-}$ or $C_2O_4^{\cdot-}$. An approximate theoretical calculation[5)] indicates that the latter radical is more stable, but the two forms do not appear to be distinguishable on the basis of kinetic or spectroscopic evidence.[6)] Conveniently we write $CO_2^{\cdot-}$ in this paper. In this paper, in which all the experiments were carried out in acid media, considerations must be taken of the protonated and dissociated forms of the anion species. According to the data by Fojtik *et al.*,[7)] the acid dissociation constant for the reaction $HCO_2^{\cdot} \rightleftarrows CO_2^{\cdot-} + H^+$ is $pK_a = 3.9$. Therefore, in 0.1 M sulfuric acid solutions such as in Tables 1 and 2, a predominant species of radicals is assumed to be $HCO_2^{\cdot}$. By a similar calculation for the protonated and dissociated forms of oxalate, $H_2C_2O_4$ is assumed as a predominant species. Consequently, in subsequent equations $HCO_2^{\cdot}$ and $H_2C_2O_4$ are written rather than $CO_2^{\cdot}$ and $C_2O_4^{2-}$.

Following after the initiation reactions (1) and (2), reactions, (3), (4), and (5) constitute a chain reaction.

$$HgCl_2 + HCO_2^{\cdot} \longrightarrow Hg(I) + H^+ + 2Cl^- + CO_2 \quad (3)$$

$$H_2C_2O_4 + Hg(I) \longrightarrow Hg + HCO_2^{\cdot} + CO_2 + H^+ \quad (4)$$

$$HgCl_2 + Hg \longrightarrow Hg_2Cl_2 \quad (5)$$

Termination presumably occurs mainly *via*

$$Hg(I) + HCO_2^{\cdot} \longrightarrow Hg + CO_2 + H^+ \quad (6)$$

Assumption of the steady state concentrations for HCO_2, Hg (I), and Hg, together with the assumption that the chain is long, leads to the following equation.

$$[Hg_2Cl_2]_{formed} = \sqrt{\frac{k_0 k_3 k_4 [HgCl_2][H_2C_2O_4][Co(C_2O_4)_3^{3-}]}{2k_6}}\ \tau \quad (7)$$

where k_0 indicates an overall decomposition-rate constant of trioxalatocobaltate (III), k_n, the rate constant of reaction (n), and τ, the reaction time. When the initial concentrations of oxalic acid and mercury (II) chloride are much larger than the concentrations of mercury (I) formed, the former concentrations remain approximately constant during the reaction time. Under these circumstances, Eq. (7) predicts a linear relation between $[Hg_2Cl_2]_{formed}/[Co(C_2O_4)_3^{3-}]^{1/2}$ and τ. This relation was found experimentally at all the experiments. Several examples obtained at the various temperatures are given in Fig. 1. The slopes of the straight lines in Fig. 1 correspond to the apparent-overall rate constants, *i.e.*, $k_{app} = \{k_0 k_3 k_4/(2k_6)\}^{1/2}$. From Arrhenius plots with respect to k_{app} and k_0, activation energies for the overall and initiation reactions were determined to be $E_{app} = 28$ kcal/mol, and $E_0 = 39$ kcal/mol, respectively. From the relation between the overall rate constant and the rate constants for the separate steps in the reaction scheme, the activation energy of the overall reaction constitutes a function with the activation energies for the separate steps in reaction, *i.e.*, $2E_{app} = E_0 + E_3 + E_4 - E_6$. If the activation energy for the termination reaction (6) is assumed to be negligibly small, the activation energy for the chain propagation steps is calculated to be $E_3 + E_4 = 17$ kcal/mol.

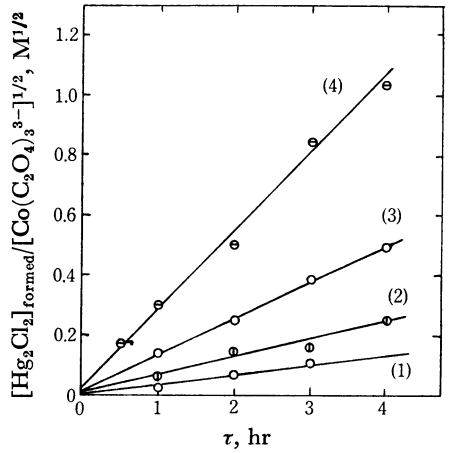

Fig. 1. Plot of $[Hg_2Cl_2]_{formed}/[Co(C_2O_4)_3^{3-}]^{1/2}$ *vs.* τ. Conditions as in Table 2. Temperatures are 25 °C (1), 30 °C (2), 35 °C (3), and 40 °C (4).

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