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The Carbon-catalyzed Oxidation of Co(II)-Ethylenediaminetetraacetate by Molecular Oxygen

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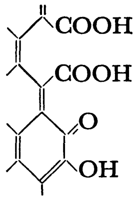
The kinetics of the oxidation of a cobaltous complex of ethylenediaminetetraacetic acid (EDTA) is determined volumetrically at 50.0°C in the presence of several kinds of carbon as catalysts. One mole of oxygen was used to oxidize four Co(II) ions, and all the Co(II) ions were oxidized to $Co(EDTA)^-$ ions quantitatively. The rate of oxygen uptake was found to change from zeroth order to first order with respect to the complex ion during the course of oxidation; it was also found to be first order with the oxygen pressure and the amount of the carbon catalyst. The catalytic activity of the carbon was correlated to the quantity of surface basic oxides of the carbon. A possible mechanism which can account for the above results is proposed.

Many reactions have been known to be catalyzed by carbons or metals supported on carbon.[1] Several works[2-4] have also described the catalytic effect of the carbon on the reaction of coordination compounds, but no mechanistic details have been investigated. Recently, the functional groups on the carbon surface have been characterized by various methods. The presence of acidic oxides I[5] and basic oxides II[6] has been reported. As a first step to studying the interaction between metal complex ions and the carbon, we previously studied[7] the adsorption of a $Co(NH_3)_6^{3+}$ ion onto carbon and the base hydrolysis of the same complex ion catalyzed by the carbon. In that paper, we concluded that the active site was the acidic oxide on the carbon surface I, and suggested that the electrostatic force between the complex ion and the acidic oxides is one of the most important factors in their interaction. It then appeared of interest to investigate whether or not the active site for the reaction of complex *anions* was also the acidic oxide. The oxidation of a Co(II)-EDTA complex was undertaken for this purpose.



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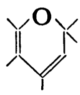

II

A Co(II)-EDTA complex ion has been known to be oxidized by various oxidants, such as H_2O_2, PbO_2,[8] and $Fe(phen)_3$.[9] It cannot be oxidized in an aqueous

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[5] H. P. Boehm, *Angew. Chem.*, **76**, 742 (1964); *ibid.*, **78**, 617 (1966).

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solution by bubbling oxygen or air. During the course of the previous investigation, we found the catalytic activity of the carbon for the air-oxidation of this complex ion. The catalytic effect of the carbon on the oxidation reaction has been reported in the cases of a $Co(NH_3)_6^{2+}$ ion[10] and a Fe^{2+} ion[11] with no explanation of the role of the catalyst. This paper will report the results of a kinetic study of the oxidation of the Co(II)-EDTA ion, and a tentative mechanism for the oxidation will be discussed in relation to the functional groups on the carbon surface.

Experimental

Reagents. A solution of Co(II)-EDTA was prepared from cobaltous nitrate and disodium salt of EDTA unless otherwise stated; the pH of the solution was about 0.7. The predominant chemical species under these conditions has been identified as $Co(HL)(H_2O)^-$, where L indicates the ethylenediaminetetraacetate ion.[12] The effect of the initial pH of the solution was determined in a medium with an ionic strength of 1.0 μ ($NaNO_3$). The hydrogen ion concentration was adjusted by the addition of a dilute sodium hydroxide solution.

Two kinds of carbons with different surface areas were used: a carbon black (HAF) and an active carbon (AC). These carbons were modified by the method of Boehm.[5] The surface area (N_2 adsorption) and the surface acidity (NaOH consumption) are listed in Table 1. The pretreatment of the carbon is designated by an appended "n" or "o" for oxidation by HNO_3 or O_2 respectively.

Kinetic Measurement. We used a general type of apparatus, incorporating a constant-pressure gas buret with a volume of 50 m*l* and a reaction flask with a stirrer driven magnetically. The reaction flask held 40 m*l* of the reacting solution. The flask had a side chamber containing 10 g of soda lime to absorb the carbon dioxide produced. After the aqueous solution had been saturated with oxygen and allowed to come to the desired temperature, the reaction was started by plunging the carbon catalyst under a stream of oxygen and adjusting the pressure of oxygen. The gas buret was placed in a constant-temperature bath which was held at 30.0°C, while the reactor was kept in a bath maintained at 50.0°C. They were then placed in a room which was also thermostated at 27.2°C. The rate of oxidation was measured by the amount of oxygen absorbed during the course of oxidation.

Results

Typical profiles of the oxygen absorption are shown in Fig. 1. The plateau region of these curves corresponds to 95—102% of complete oxidation calculated on the basis of:

$$4Co(HL)(H_2O)^- + O_2 \longrightarrow 4CoL^- + 6H_2O \quad (1)$$

The absorption spectrum of the solution corresponding to this stage also shows that all the cobalt ions are present as forms of the CoL^- ion. These curves were obtained in the presence of soda lime in the side compartment of the flask. Otherwise, the gas absorption curve falls again due to the evolution of carbon dioxide after the absorption of oxygen of this molarity. The evolution of carbon dioxide may be attributed to the formation of the CoL^- ion in the first step, because this phenomenon was also observed when we used the CoL^- ion instead of the $Co(HL)(H_2O)^-$ ion as the starting material. Figure 1 illustrates the effect of the initial concentration of the complex ion on the rate. The initial slopes of all the curves are equivalent, in spite of the different initial concentrations. This fact and the linearity over the initial range indicate that the reaction is of the zeroth order. Deviation from linearity occurs later, since the kinetics approaches first-order behavior.

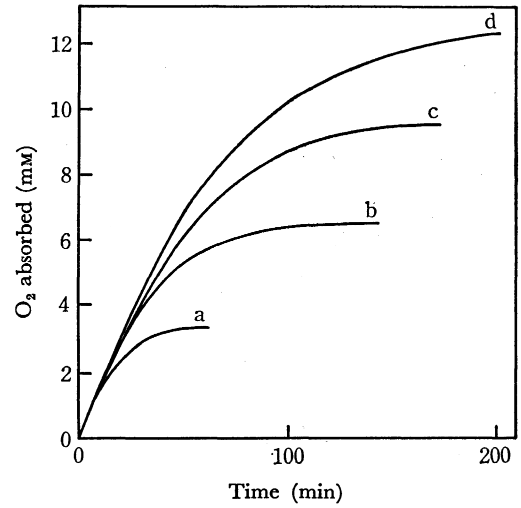

Fig. 1. Effect of initial concentration of Co(II)-EDTA: (a) 12.5 mM; (b) 25 mM; (c) 37.5 mM; (d) 50 mM. Carbon, AC 200 mg; Temperature, 50.0°C; Oxygen, 700 mmHg.

The zeroth-order rate constant as a function of the amount of the carbon was found to vary linearly in the range of 0—500 mg (Fig. 2). Such a dependence is expected for a solid catalyst, the rate being a function of the number of active sites on the surface. The rate

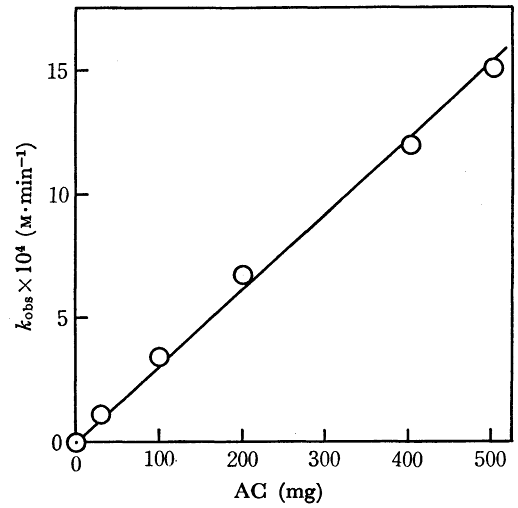

Fig. 2. Effect of the amount of AC at 50.0°C. Co(II)-EDTA, 50 mM; Oxygen, 700 mmHg.

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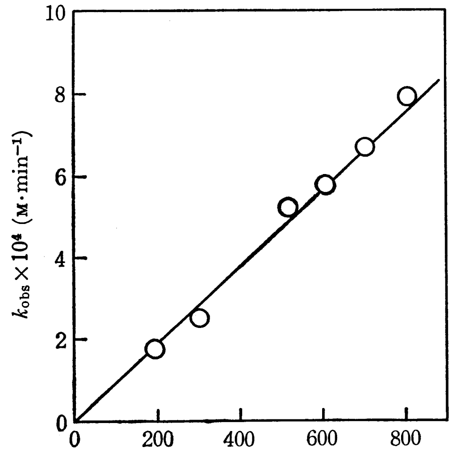


Fig. 3. Effect of the oxygen pressure at 50.0°C. Co(II)-EDTA, 50 mM; Carbon, AC 200 mg.

in the absence of the carbon was extremely low. Figure 3 shows the linear variation of the rate constant with the oxygen pressure. No oxidation was observed when the atmospheric gas was replaced by nitrogen.

The effect of the initial pH of the solution was determined in the pH region from 0.7 to 1.2, and the observed zeroth-order rate constant was represented by:

$$k_{obs} = k_a + k_b/[\mathrm{H}^+] \qquad (2)$$

and $k_a=7\times10^{-4}$ (M·min^{-1}) and $k_b=0.3\times10^{-4}$ (M^2·min^{-1}) are obtained at 50.0°C.

The rate constants given in Table 1 were obtained by using carbons with different surface acidities or basicities. In these runs, some experimental conditions were different from those mentioned above: cobaltous chloride was used for preparing the starting material, and the reaction temperature was 30.0°C. The catalytic activity of carbons is well correlated with the surface basicity (see also Fig. 4), but not with the surface acidity. This tendency is quite in contrast with the case of the *cationic* complex ion.[7] Under these conditions, the effect of the temperature was investigated only briefly. One oxidation run catalyzed by AC was made at 50.0°C; we found that k_{obs} was 8.6×10^{-4} (M·min^{-1}). The apparent activation energy was calculated to be about 9 kcal/mol.

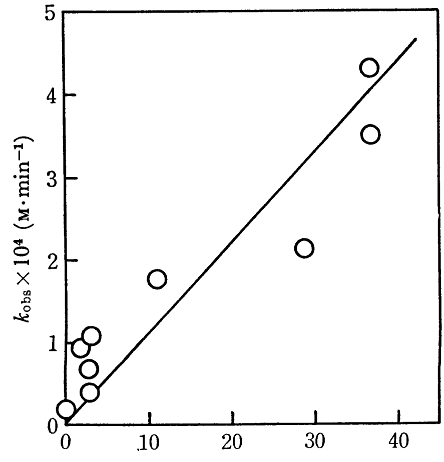


Fig. 4. Relationship between the rate constant and the basicity of the carbon surface.

Table 1. Observed rate constants for the oxidation of $\mathrm{Co(HL)(H_2O)^-}$ catalyzed by various carbons[a)]

Carbon	Surface Area (m^2/g)	Acidity[b)] (meq/100g)	Basicity[c)] (meq/100g)	$k_{obs}\times10^4$ (M·min^{-1})
AC-o1	1120	38.7	37	4.3
AC	1230	32.7	37	3.5
AC-n3	—	111	29	2.1
AC-o2	1100	118	11	1.75
HAF	81	2.2	3	1.1
HAF-n3	82	5.7	2	1.0
HAF-n6	—	12.5	3	0.71
HAF-n4	71	14.7	3	0.42
HAF-o1	170	40.1	0	0.24

a) Co(II)-EDTA, 50 mM; Carbon, 200 mg; Oxygen, 700 mmHg; Temperature, 30.0°C.
b) NaOH consumption.
c) HCl consumption.

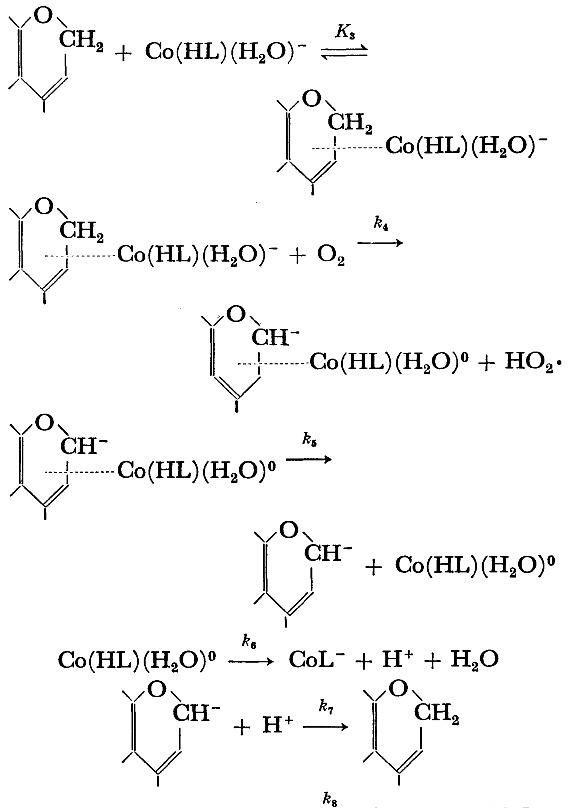
Discussion

Carbon dioxide evolution after the formation of the CoL$^-$ ion may be considered to arise from the oxidation of carbon or from the decarboxylation of the EDTA complex. We regard the former as unlikely. Evidence in favor of the latter was adduced from the experiments in gas evolution starting from the CoL$^-$ ion: (1) carbon dioxide was also observed to evolve under a nitrogen atmosphere, (2) the absorbance at 537 mμ corresponding to the CoL$^-$ ion decreased upon the evolution of carbon dioxide, and (3) the amount of carbon dioxide evolved was closely related to the initial concentration of the CoL$^-$ ion. As a more detailed mechanism is not clear from the data now available, we would like to limit our discussion to the first step of oxidation, where the side reaction is considered to be slow enough.

Any mechanism proposed for the carbon-catalyzed oxidation of a Co(II)-EDTA complex must explain, or be in accord with, the dependences of the rate on the following: (1) the amount of the carbon, (2) the oxygen pressure, (3) the initial concentration of a Co(II) complex, (4) the pH of the solution, and (5) the surface acidity or basicity of the catalysts. As there is an inverse correlation between the acidity of the carbon and the activity, the adsorption of a Co(II) complex on the acidic-surface oxides I is unlikely. Although this inverse correlation can be explained by the electrostatic repulsion between the dissociated acidic groups (*i.e.*, the -COO$^-$ or -O$^-$ group) and the complex anions, this interpretation is inadequate because these acidic groups are not dissociated because of the low pH value of the solution. On the other hand, the activity of carbon was well correlated with the quantity of basic surface oxides, and it seems reasonable to conclude that the active sites for this oxidation are those basic oxides (*i.e.*, with the chromene-type structure II). The following scheme may be proposed to account for the catalytic action of these functional groups:

$$O_2(\text{gas}) \overset{K_1}{\rightleftharpoons} O_2(\text{solution})$$

$$Co(HL)(H_2O)^- \overset{K_2}{\rightleftharpoons} CoL(H_2O)^{2-} + H^+$$



$$Co(HL)(H_2O)^0 \xrightarrow{k_6} CoL^- + H^+ + H_2O$$

$$3Co(HL)(H_2O)^- + HO_2\cdot \xrightarrow{k_8} 3CoL^- + 5H_2O$$

The oxidation reaction seems to proceed through two simultaneous reaction paths, one of which involves the oxidation of the protonated chelate as described above, while the other involves the oxidation of the unprotonated chelate, $CoL(H_2O)^{2-}$. The corresponding constants for $CoL\ (H_2O)^{2-}$ will be marked K_3', k_4', k_5', and k_6' in the following discussion. Although the presence of a sexidentate CoL^{2-} has been suggested,[9] it seems reasonable to consider only two quinquedentate anions represented by the K_2 equilibrium in a strongly acidic solution.[9,12] Letting the fraction of the surface sites covered with $Co(HL)(H_2O)^-$ and $CoL(H_2O)^{2-}$ be θ and θ', and letting the total concentration of Co-(II) complexes be represented by $[Co]_T$, one obtains:

$$K_3 = \frac{\theta}{(1-\theta-\theta')\cdot[Co(HL)(H_2O)^-]} = \frac{\theta\cdot([H^+]+K_2)}{(1-\theta-\theta')\cdot[H^+]\cdot[Co]_T} \quad (3)$$

and:

$$K_3' = \frac{\theta'\cdot([H^+]+K_2)}{(1-\theta-\theta')\cdot K_2\cdot[Co]_T} \quad (4)$$

where K_3 and K_3' are the equilibrium constants for the adsorption of complex ions on the carbon. The adsorption is followed by an attack of oxygen; this is the rate-determining step, k_4 or k_4'. Assuming that the rate of $[Co(II)]_T$ consumption equals four times the rate of oxygen consumption, we can express the rate of oxidation by the above pathway as:

$$-d[Co]_T/dt = -4d[O_2]/dt = (k_4\theta+k_4'\theta')\cdot[C]\cdot K_1\cdot P \quad (5)$$

where [C] is the "concentration" of the carbon catalyst and where P is the oxygen pressure in the gas phase. Combining Eqs. (3), (4), and (5) gives:

$$-d[Co]_T/dt = \frac{(k_4\cdot K_3\cdot[H^+]+k_4'\cdot K_3'\cdot K_2)\cdot[Co]_T}{[H^+]+K_2+(K_3\cdot[H^+]+K_3'\cdot K_2)\cdot[Co]_T} \times[C]\cdot K_1\cdot P \quad (6)$$

This equation can explain the fact that the reaction is zeroth-order with respect to $[Co]_T$ at the beginning of the oxidation and is first-order at lower concentrations of the cobaltous ion. Equation (6) also shows a simple dependence of the rate of oxidation on the oxygen pressure and the amount of the carbon catalyst. The validity of this relationship may be seen by the same dependences shown in Figs. 2 and 3. The effect of the pH on the zeroth-order rate constant shown in Eq. (6) may be expressed in the form:

$$k_{obs} = K\cdot\frac{k_4\cdot K_3\cdot[H^+]+k_4'\cdot K_3'\cdot K_2}{K_3\cdot[H^+]+K_3'\cdot K_2} \quad (7)$$

where K is $[C]\cdot K_1\cdot P$, which was kept constant in these runs. In a strongly acidic solution, where $K_3'\cdot K_2$ is small compared to $K_3\cdot[H^+]$, Eq. (7) simplifies to:

$$k_{obs} = K\cdot\left(k_4+\frac{k_4\cdot K_2\cdot K_3'/K_3}{[H^+]}\right) \quad (8)$$

This theoretical equation agrees with the experimental equation (2). The dissociation constant, K_2, was reported[12] to be approximately 10^{-3}. Using this value and the constants presented in Eq. (2), we can estimate the $k_4\cdot K_3/k_4'\cdot K_3'$ ratio to be 0.023. The fact that this ratio is smaller than unity may be understood if one considers that the rate of the electron transfer to produce a pair of anions (k_4') might be faster than k_4. The oxidized complex ions may then be dissociated from the carbon surface in a fast step (k_5 and k_5'). The dehydration of the quinquedentate complex ion into the sexidentate CoL^- ion may then take place in a subsequent fast step (k_6). Considering the data reported[13] below 25°C, we can estimate the rate of this step to be very large compared to the preceeding steps. The $HO_2\cdot$ radical produced in the rate-determining step oxidizes the other three ions of Co(II)-EDTA accoring to the Weiss mechanism[14] (k_8). Thus, four ions of Co(II)-EDTA complexes are oxidized by one molecule of oxygen.

In conclusion, it should be emphasized that the catalytic behavior of the carbon in connection with the oxidation of Co (II)-EDTA was quite different from that for the adsorption or the hydrolysis of the $Co(NH_3)_6{}^{3+}$ ion. The active sites for the former case were surface basic oxides, II, whereas those for the latter were surface acidic oxides, I. Whether this difference has arisen from the electric charge of the complex ions, from the choice of different types of reactions, or from other reasons is not yet clear; it is advisable to investigate other reactions[15] in order to elucidate this point.

The author is grateful to Professor Yasukatsu Tamai for his helpful discussions.

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