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Kinetics and Mechanisms of a New Type of Catalysis in the Activated Carbon for the Ligand-Substitution Reaction between the Inert Complex $[Co(NH_3)_5Cl]^{2+}$ and EDTA in Aqueous Media

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The ligand-substitution reaction of the pentaamminechlorocobalt(III) ion, $[Co(NH_3)_5Cl]^{2+}$, with ethylenediaminetetraacetate (EDTA) (which denotes all the forms of EDTA, i.e. $edta^{4-}$, $Hedta^{3-}$, H_2edta^{2-} etc.) occurred efficiently in the presence of the activated carbon (AC) in aqueous media of pH 4.7, where the AC acts as a catalyst of the electron-transfer mediator. The ligand-substitution reaction constitutes a chain reaction composed of an AC and AC^+ cycle, where the substitution reaction is initiated by the electron-transfer from AC to the cobalt(III) complex. The formation rate of $[Co(edta)]^-$ by the substitution reaction between $[Co(NH_3)_5Cl]^{2+}$ and EDTA was of the first-order with respect to concentrations of not only $[Co(NH_3)_5Cl]^{2+}$ but also AC, and was of the zero-order with respect to the EDTA concentration. Further, the rate was irrespective of the dissolved oxygen O_2. The substitution reaction was always quantitative, i.e. $[[Co(NH_3)_5Cl]^{2+}]_{decreased}=[[Co(edta)]^-]_{formed}$ at any reaction time up to completion of reaction.

The activated carbon (AC) has been widely known as an adsorbent in a variety of decolorizations, deodorizations, gas separations, and catalysts, and the reducing properties of the AC have been also known for long time.[1] However, the reaction mechanisms of AC as the reducing properties have been scarcely reported yet. We believe that the present work is the first discovery of AC as the electron-transfer mediator composed of an AC and AC^+ cycle, where AC^+ is a cation radical in the surface of the powder-particle.

In our previous work,[2] the photo-induced ligand substitution reaction between $[Co(NH_3)_5Cl]^{2+}$ and EDTA by irradiation with visible light of aqueous solutions containing the tris(2,2′-bipyridine)ruthenium(II) was reported, where the ruthenium(II) complex ion was a photo-catalyst. Thus, AC in the present work is comparable to the ruthenium(II) complex in the previous work.[2] Our present results show that the AC is a very excellent electron-transfer mediator in an AC/AC^+ cycle in situ on the surfaces of the AC powder-particles.

Experimental

Reagents. Activated carbon (Wako Pure Chemical Co. Ltd.) was stirred to wash with 1 M ($M=mol\,dm^{-3}$) hydrochloric acid for 3—4 h; it was then washed throughly with distilled water, kept over night in distilled water and then filtered. The AC obtained was dried at 100—120 °C. The AC powder used are over 100 mesh (over 90% passed through the 100 mesh filter). $[Co(NH_3)_5Cl]Cl_2$ was prepared as described in the literature[3] and recrystallized twice. Disodium dihydrogen ethylenediaminetetraacetate ($Na_2[H_2edta]$) and other chemicals used were of guaranteed-reagent grade. Deionized water was further distilled in a glass still.

Procedure. The reaction was initiated by adding the AC into solutions of 100 cm^3 containing an acetate buffer of pH 4.7, $[Co(NH_3)_5Cl]^{2+}$ and EDTA. The reaction mixture was always stirred rigorously with a magnetic stirrer in order to make a homogeneous suspension of the AC powder for the times given.

After filtration, concentrations of $[Co(NH_3)_5Cl]^{2+}$ remaining and $[Co(edta)]^-$ formed were determined spectrophotometrically by using the molar absorption coefficients 51.3 $M^{-1}\,cm^{-1}$ at 534 nm and 295 $M^{-1}\,cm^{-1}$ at 536 nm, respectively. On the other hand, aliquot solutions of 5 cm^3 after the removal of AC were for one minute mixed with cation-exchange resin of 1 g (Dowex 50W-X8; 200—400 mesh, hydrogen form of the Wako Pure Chemical Co., Ltd., washed with distilled water) in order to remove the $[Co(NH_3)_5Cl]^{2+}$ ion. After filtration, the concentration of the $[Co(edta)]^-$ formed was determined spectrophotometrically at 536 nm.

Results and Discussion

As seen in Table 1, concentrations of $[Co(edta)]^-$ formed and $[Co(NH_3)_5Cl]^{2+}$ disappeared are equal at any time of reaction. As seen in Fig. 1 the rate of decrease of $[Co(NH_3)_5Cl]^{2+}$ is of the first-order up to completion of reaction. The rate constants of the first-order plots increased proportionally to the amounts of the AC added (see Table 2). Thus, the rates of either formation of $[Co(edta)]^-$ or decrease of $[Co(NH_3)_5Cl]^{2+}$ are of the first-order with respect to not only the $[Co(NH_3)_5Cl]^{2+}$ concentration, but also the surface-area of the AC. What the linear plots such as in Fig. 1 continued up to completion of reaction indicates no remarkable change in the activities of AC during the reaction times and indicates also the AC catalysis for the electron-transfer and the reaction mediator (or carrier) of electron. As seen in Table 3, the catalyzed reaction rate was independent of the molecular oxygen. The results in Table 3 indicate that the oxygen is indifferent to the catalytic action in the present reaction. The zero-order dependence with respect to the EDTA concentrations (Fig. 2) indicates that the rate determining step is the formation of AC^+ and $[Co(edta)]^{2-}$, and that the electron-transfer between AC^+ and $[Co(edta)]^{2-}$ occurs in situ to form rapidly the $[Co(edta)]^-$ (see Scheme 1).

Table 1. Concentrations Reacted by the AC Catalyzed Reaction[a)]

t	$[\mathrm{Co(NH_3)_5Cl}]^{2+}_{\mathrm{disapp.}}$			$[\mathrm{Co(edta)}]^{-}_{\mathrm{formed}}$			$[\mathrm{Co(edta)}]^{-}_{\mathrm{formed}}$		
min	10^{-3} M			10^{-3} M			$[\mathrm{Co(NH_3)_5Cl}]^{2+}_{\mathrm{disapp.}}$		
5	0.78	0.92[b)]	1.17[c)]	0.74	0.84[b)]	1.23[c)]	0.95	0.91[b)]	1.05[c)]
10	1.27	1.33[b)]	2.13[c)]	1.26	1.29[b)]	2.05[c)]	0.99	0.97[b)]	0.96[c)]
20	1.72	1.74[b)]	2.79[c)]	1.72	1.73[b)]	2.78[c)]	1.00	0.99[b)]	1.00[c)]
30		2.53[b)]	4.21[c)]		2.60[b)]	4.46[c)]		1.03[b)]	1.06[c)]
40	3.10	2.75[b)]		3.27	3.12[b)]		1.05	1.13[b)]	
50		3.65[b)]			3.79[b)]			1.04[b)]	
60	3.80	3.70[b)]	4.72[c)]	4.14	3.92[b)]	5.01[c)]	1.09	1.06[b)]	1.06[c)]
90	4.37			4.89			1.12		
							Av. 1.03±0.06		

a) Conditions are the same as in Fig. 1. b) Data in 1.0×10^{-2} M EDTA; other conditions are as in a). c) Data in 100 mg/100 cm^3 of AC; other conditions are as in a).

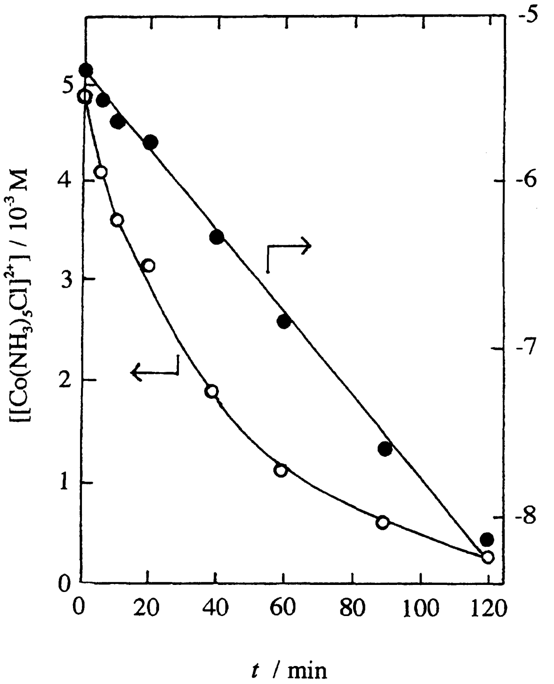
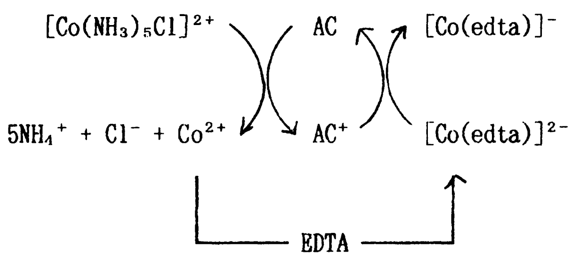


Fig. 1. First-Order plots. Conditions: 4.9×10^{-3} M $[\mathrm{Co(NH_3)_5Cl}]\mathrm{Cl_2}$, 5.0×10^{-3} M $\mathrm{Na_2[H_2edta]}$, 0.05 M $\mathrm{CH_3COOH{-}CH_3COONa}$ (pH 4.7) and at room temperature (20—23 °C); AC=50 mg/100 cm^3.

Table 2. Dependence of the AC Amounts on the First-Order Rate Constants[a)]

AC/mg per 100 cm^3	$k_{\mathrm{obsd}}/10^{-4}\mathrm{s}^{-1}$
0	0.000
5	0.187
20	0.913
50	4.13
70	4.83
100	9.45

a) Conditions are the same as in Fig. 1.



Scheme 1.

This affords the rate law of $-\mathrm{d}[[\mathrm{Co(NH_3)_5Cl}]^{2+}]/\mathrm{d}t = k_{\mathrm{obsd}}[[\mathrm{Co(NH_3)_5Cl}]^{2+}]$ where k_{obsd} is proportional to the AC amount (i.e. surface area of AC), expressed by the rate law of $k_{\mathrm{obsd}}=kK[\mathrm{AC}]/(1+K[\mathrm{AC}])=kK[\mathrm{AC}]$ under conditions of $K[\mathrm{AC}]\ll1$, where K is the equilibrium constant of the electron-transfer reaction between AC and $[\mathrm{Co(NH_3)_5Cl}]^{2+}$, and k is rate constant of the oxidation reaction of $[\mathrm{Co(edta)}]^{2-}$ by AC^{+}.

Reaction Mechanism. The following mechanism of reaction given in Scheme 1 is postulated to account for the results obtained.

The reduction of $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ by AC and the successive formation of the $[\mathrm{Co(edta)}]^{2-}$ and its oxidation by AC^{+} to $[\mathrm{Co(edta)}]^{-}$ should occur in situ on the AC surface. It is obvious that the oxidation of AC to AC^{+} by the $[\mathrm{Co(edta)}]^{-}$ does not occur at all because of no deviation in plots of $\ln[[\mathrm{Co(NH_3)_5Cl}]^{2+}]$ vs. t up to completion of reaction (see Fig. 1). This matter was further confirmed under the runs of excess EDTA over $[\mathrm{Co(NH_3)_5Cl}]^{2+}$: When the reaction solution of 3.0 mM $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ and 6.0 mM EDTA at pH 4.7 was mixed with 100 mg of AC to start the reaction in the same way as in Figs. 1 and 2, the concentrations of $[\mathrm{Co(edta)}]^{-}$ formed were 2.4, 2.7, 3.1, 2.7, 2.8, and 2.9 mM at the reaction times of 30, 60, 80, 90, 120, and 150 min, respectively. This indicates $[[\mathrm{Co(edta)}]^{-}]_{\mathrm{formed}}=1/2\text{-}[\mathrm{EDTA}]_{\mathrm{added}}=[[\mathrm{Co(NH_3)_5Cl}]^{2+}]_{\mathrm{added}}$ after t=60—150 min, and that the concentrations of $[\mathrm{Co(edta)}]^{-}$ formed do not change appreciably. Therefore, it is assumed that there is no oxidation of AC to AC^{+} by the $[\mathrm{Co(edta)}]^{-}$, which may be accompanied with the oxida-

Table 3. Independence of the Molecular Oxygen Dissolved[a)]

t/min	$[Co(NH_3)_5Cl]^{2+}_{disapp.}/10^{-3}$ M		$[Co(edta)]^{-}_{formed}/10^{-3}$ M	
	N_2-sat.	O_2-sat.	N_2-sat.	O_2-sat.
30	2.54	2.29	2.61	2.42
60	3.82	3.64	3.79	3.77

a) Conditions are the same as in Fig. 1.

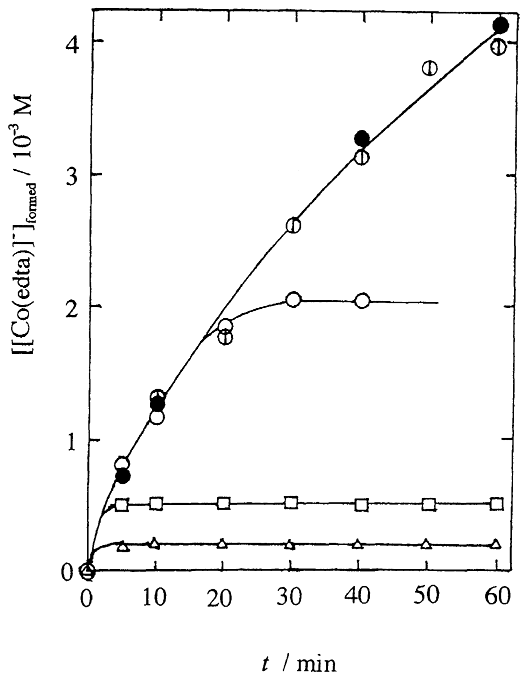


Fig. 2. Effect of the EDTA concentration on the formation rate of $[Co(edta)]^{-}$. EDTA at $t=0$ are 2×10^{-4}, 5×10^{-4}, 2×10^{-3}, 5×10^{-3}, and 1×10^{-2} M for plots △, □, ○, ●, and ⦶, respectively. Other conditions are as in Fig. 1.

tion of EDTA by AC^{+}. Consequently, the AC can operate as the most ideal electron-mediator composed of a chain reaction without taking termination reaction. That the $[Co(NH_3)_5Cl]^{2+}$ did not decrease in the absence of EDTA indicates that the AC^{+} consumption is absolutely necessary in order to act as an electron-mediator catalysis in the AC. We believe that many types of oxidation reactions using AC^{+} can be designed by using the AC. It might be wonderful that the AC could be oxidized to AC^{+} by the $[Co(NH_3)_5Cl]^{2+}$ ion which is rather an weak oxidant.

As far as the Scheme 1 is concerned, it is comparable to the scheme in our previous study[2)] of the photo-induced ligand-substitution reaction between $[Co(NH_3)_5Cl]^{2+}$ and EDTA by using $[Ru(bpy)_3]^{2+}$ which is a photo-catalyst. It is to be noted here that the AC/AC^{+} cycle in this study corresponds to the $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$ cycle in the previous work[2)] and that the AC^{+}, in contrast to the $[Ru(bpy)_3]^{3+}$, is not capable of oxidizing EDTA.

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