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Discovery of the Activated-Carbon Radical AC^+ and the Novel Oxidation-Reactions Comprising the AC/AC^+ Cycle as a Catalyst in an Aqueous Solution

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The oxidation reaction of the cobalt(II) complex $[Co(edta)]^{2-}$ to $[Co(edta)]^-$ ($edta^{4-}$=ethylenediaminetetraacetate ion) occurred efficiently by hydrogen peroxide or peroxodisulfate with activated carbon (AC) in aqueous media of pH 4.7, where the AC acts as a catalyst of the electron-transfer mediator. The oxidation reaction constitutes a chain reaction comprising the AC/AC^+ cycle, in which the oxidation reaction is initiated by an electron-transfer from AC to hydrogen peroxide or peroxodisulfate to make radicals of AC^+ and $OH^\bullet$, or $SO_4^{-\bullet}$. These radicals could rapidly oxidize $[Co(edta)]^{2-}$ to $[Co(edta)]^-$. The rate of the oxidation reaction is of first-order with respect to the concentrations of hydrogen peroxide (or peroxodisulfate) and the AC amounts added, and of zero-order to $[Co(edta)]^{2-}$ under the conditions. Further, the rate was unrelated to the dissolved O_2. In the case of hydrogen peroxide, it could be decomposed by the AC, even in the absence of $[Co(edta)]^{2-}$, according to the first-order with respect to the hydrogen peroxide concentration; the rate constant was 2-fold of the rate constant in the presence of $[Co(edta)]^{2-}$. However, in the case of peroxodisulfate, no appreciable decomposition of the $S_2O_8^{2-}$ was found in the absence of $[Co(edta)]^{2-}$, and the decomposition rate in the presence of $[Co(edta)]^{2-}$ was 10^4-fold faster than the rate of hydrogen peroxide decomposition under the same conditions. Consequently, it is concluded that the AC acts in a way similar to iron(II) ion in the Fenton-reagent.

Activated carbon (AC) has been widely known as adsorbents in a variety of decolorizations, deodorizations, gas separations, and catalysts. The reducing properties of AC have also been known for long time.[1] However, the reaction mechanisms of AC as the reducing properties have to date been scarcely solved. We believe that the present work represents the first discovery of AC as an electron-transfer mediator involving the AC and AC^+ cycle, where AC^+ reveals the oxidizing cation-radical properties which constitute the Haber–Weiss mechanism.[2] Thus, the AC used in the present work is comparable to the iron(II) ion in the Fenton-reagent.[3] The present results concerning Fenton-like reagents should be applicable to many kinds of the oxidation reactions. Especially, the AC/AC^+ cycle with $S_2O_8^{2-}/SO_4^{-\bullet}$ is not only a very strong oxidizing reagent, but is also a fast reaction, and will be useful in practice as well. Although Fenton-like reagents, e.g. Ti^{3+}/H_2O_2, $Ti^{3+}/S_2O_8^{2-}$, Ti^{3+}/NH_2OH, V^{4+}/H_2O_2, Ce^{4+}/H_2O_2, and so forth, have been known,[4] both the AC/H_2O_2 and $AC/S_2O_8^{2-}$ mentioned in this article are not yet known.

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, washed throughly with distilled water and left standing over night in distilled water, and then filtered. The AC obtained was dried at 100—120 °C. The powder of the AC used was 100 mesh (over 95% passed through a 100-mesh filter). 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. (1) In the case of the decomposition reaction of hydrogen peroxide with AC, the reaction was initiated by adding the AC into 100 cm^3 solutions containing an acetate buffer of pH 4.7 and hydrogen peroxide. The reaction mixture was always stirred rigorously with a magnetic stirrer in order to make a homogeneous suspension of the AC powder-particle for the given times. After filtration, the aliquot solutions were mixed with 1 M KI and 0.01 M H_2SO_4 for 10—20 min in the dark; the formed I_3^- was then determined using a molar absorption coefficient of 2.5×10^4 $M^{-1}\,cm^{-1}$ at 350 nm.[5] (2) In the case of the oxidation reactions of $[Co(edta)]^{2-}$ to $[Co(edta)]^-$ using hydrogen peroxide with AC, although the procedures were the same as those described in (1), the solutions contained the cobalt(II) ion and EDTA, where EDTA indicates all forms of $edta^{4-}$, $Hedta^{3-}$, H_2edta^{2-} etc. concentrations of the formed $[Co(edta)]^-$ were determined spectrophotometrically at 536 nm by using the molar absorption coefficient, 295 $M^{-1}\,cm^{-1}$. On the other hand, 10 cm^3 aliquots after removing the AC were mixed for one minute with 4 g the anion-exchange resin (Dowex-X8; 50—100 mesh, Cl-Form of the Wako Pure chemical Co., Ltd., washed with distilled water) in order to remove the $[Co(edta)]^{2-}$ and $[Co(edta)]^-$. After filtration and washing well by 10 cm^3 of distilled water, aliquot solutions were mixed with 1 M KI and 0.01 M sulfuric acid for 10—20 min in the dark. Then, the formed I_3^- was determined in the same way as in (1). (3) In the case of oxidation reaction involving the peroxodisulfate ion with the AC catalysis, the procedures were the same as those in hydrogen peroxide, where $S_2O_8^{2-}$ was used in place of H_2O_2. The concentrations of the formed $[Co(edta)]^-$ were determined photometrically at 536 nm, and the concentrations of the peroxodisulfate ion remaining in the runs without $[Co(edta)]^{2-}$ were determined by the same way as in (1) for hydrogen peroxide.

Results and Discussion

As can be seen in Fig. 1, the rate of the disappearance of H_2O_2 is of first-order with respect to the hydrogen peroxide concentration, being unrelated to ei-

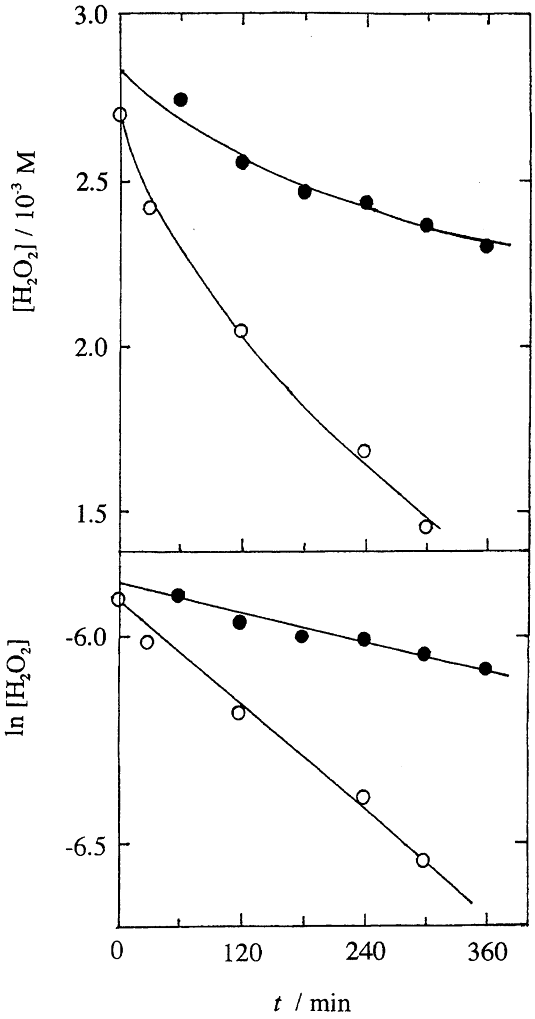

Fig. 1. First-order dependence in the H_2O_2 decompositions by the AC.
Conditions: 2.8×10^{-3} M H_2O_2, 5×10^{-3} M $[Co(edta)]^{2-}$ (i.e., $[CoSO_4]=[Na_2[H_2edta]]=5\times10^{-3}$ M), 0.05 M CH_3COOH–0.05 M CH_3COONa (pH 4.7), 500 mg AC, and at 20—23 °C for plots ●; plots ○ indicate the runs in the absence of the Co(II) complexes under the conditions as in the plots ●.

ther the absence or presence of the $[Co(edta)]^{2-}$ ion; the rate in the absence of $[Co(edta)]^{2-}$ was two-times faster than that in its presence. Thus, the rate law could be $-d[H_2O_2]/dt=(1/2)d[[Co(edta)]^-]/dt=k_{obsd}[H_2O_2]$, which increased proportionally to the amount of AC added. Thus, both the rates of formation of $[Co(edta)]^-$ and those of the H_2O_2 decomposition are of first order with respect to not only the H_2O_2 concentration, but also to the total surface area of the AC, and are of the zero-order with respect to the $[Co(edta)]^{2-}$ concentrations. These facts indicate that both the radicals of AC^+ and $OH^\bullet$ formed on the surface of AC could react rapidly with either $[Co(edta)]^{2-}$ or H_2O_2 without any other reactions with AC^+ and $OH^\bullet$, and that these radicals react predominantly with $[Co(edta)]^{2-}$. The first-order rate constants in Fig. 1, i.e., k_{obsd} are $1.0_0\times10^{-5}$ and $2.0_5\times10^{-5}$ s^{-1} in the presence and absence of $[Co(edta)]^{2-}$, respectively. In the case of the reaction of peroxodisulfate with $[Co(edta)]^{2-}$, the formation rate of $[Co(edta)]^-$ is much faster than that in the case of hydrogen peroxide, being proportional to the AC amounts (Fig. 2), and independent of the $[Co(edta)]^{2-}$ concentrations (see Fig. 3). When the reaction was started under the condition of $[[Co(edta)]^{2-}]_{t=0}=2\ [S_2O_8{}^{2-}]_{t=0}$, the plots of $\ln\{[[Co(edta)]^-]_{t=\infty}-[[Co(edta)]^-]_{t=t}\}$ vs. t were rectilinear (see Fig. 2) up to completion of the reaction. Therefore, the concentrations of $S_2O_8{}^{2-}$ decomposed are assumed to be equal to half those of $[Co(edta)]^-$ formed at any time during the reaction; both the rates of formation of $[Co(edta)]^-$ and the decomposition of $S_2O_8{}^{2-}$ are of first-order with respect to the $S_2O_8{}^{2-}$ concentration and of zero-order with respect to the $[Co(edta)]^{2-}$ concentration. The first-order rate constants for the formation of $[Co(edta)]^-$, i.e. k[AC], are $9.7_5\times10^{-4}$ and $2.0_5\times10^{-3}$ s^{-1} at 5 and 10 mg AC, respectively. The

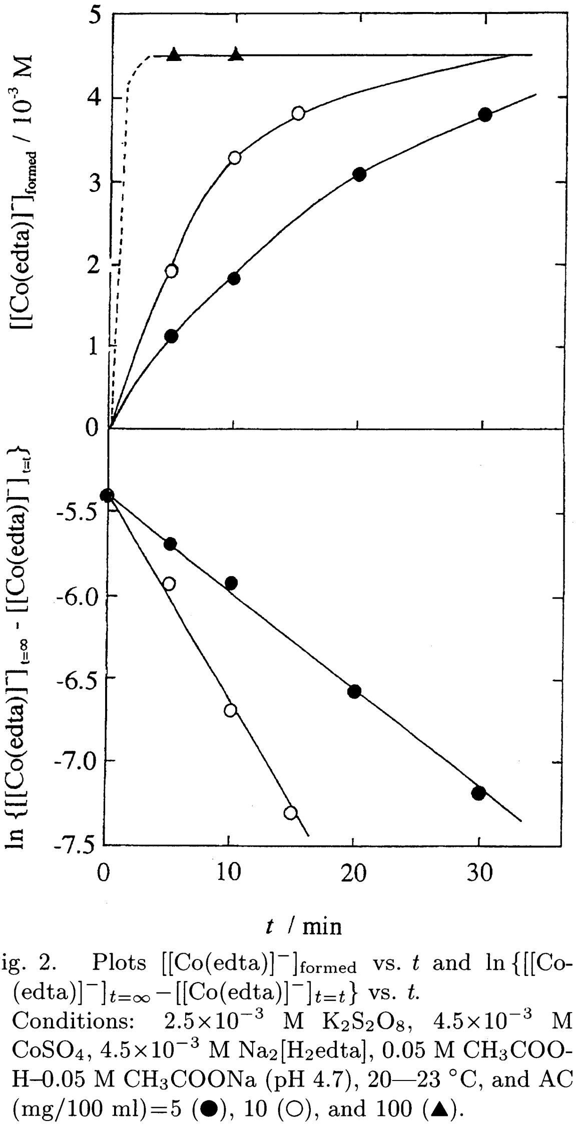

Fig. 2. Plots $[[Co(edta)]^-]_{formed}$ vs. t and $\ln\{[[Co(edta)]^-]_{t=\infty}-[[Co(edta)]^-]_{t=t}\}$ vs. t.
Conditions: 2.5×10^{-3} M $K_2S_2O_8$, 4.5×10^{-3} M $CoSO_4$, 4.5×10^{-3} M $Na_2[H_2edta]$, 0.05 M CH_3COOH–0.05 M CH_3COONa (pH 4.7), 20—23 °C, and AC (mg/100 ml)=5 (●), 10 (○), and 100 (▲).

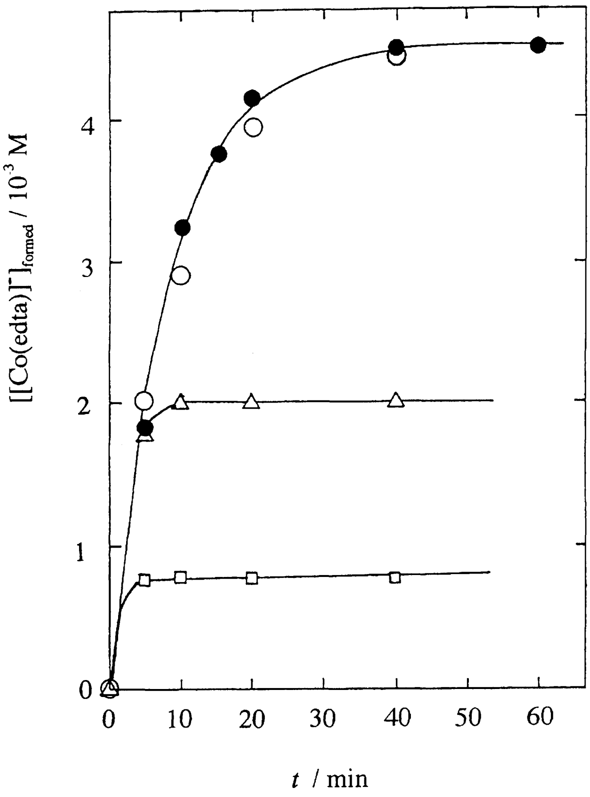

Fig. 3. Effect of concentrations of EDTA or $[Co(edta)]^{2-}$.
Conditions are the same as 10 mg AC in Fig. 2, where EDTA concentrations are 7.5×10^{-4} (□), 2.0×10^{-3} (△), 4.5×10^{-3} (●), and 1.0×10^{-2} M (○).

rate constants under the same conditions are around 10^4-times larger than those in the case of the hydrogen peroxide reactions with $[Co(edta)]^{2-}$.

Reaction Mechanisms: The following reaction mechanisms are postulated to account for the obtained results, where either reaction 1 or 7 is the rate-determining step.

$$AC + H_2O_2 \xrightarrow{k} AC^+ + OH^{\bullet} + OH^- \qquad (1)$$

In absence of $[Co(edta)]^{2-}$:

$$H_2O_2 + AC^+ \longrightarrow AC + HO_2{}^{\bullet} + H^+ \qquad (2)$$

$$H_2O_2 + OH^{\bullet} \longrightarrow HO_2{}^{\bullet} + H_2O \qquad (3)$$

$$HO_2{}^{\bullet} + OH^{\bullet} \longrightarrow H_2O + O_2 \qquad (4)$$

In presence of $[Co(edta)]^{2-}$:

$$[Co(edta)]^{2-} + AC^+ \longrightarrow [Co(edta)]^- + AC \qquad (5)$$

$$[Co(edta)]^{2-} + OH^{\bullet} \longrightarrow [Co(edta)]^- + OH^- \qquad (6)$$

The relatively slow reduction of H_2O_2 by AC and the successive fast oxidation reaction of $[Co(edta)]^{2-}$ to $[Co(edta)]^-$ by AC^+ and $OH^{\bullet}$ should occur in situ on the AC surface. Consequently, the AC could operate as an electron-carrier catalyst comprising a chain reaction of the AC/AC^+ cycle.

The above-mentioned reaction mechanisms afford the rate law, $-d[H_2O_2]/dt=2k[AC][H_2O_2]$ in the case of operating reactions 1, 2, and 4 while neglecting reaction 3 in the absence of $[Co(edta)]^{2-}$, and $-d[H_2O_2]/dt=k[AC][H_2O_2]$ in the case operating reactions 1, 5, and 6 in the presence of $[Co(edta)]^{2-}$. Consequently, the assumed rate law is in agreement with the obtained results (see Fig. 1); thus, reactions 5 and 6 could occur with dominating over reactions 2 and 3 under the specified conditions.

Thus, when the peroxodisulfate ion was used instead of hydrogen peroxide, the following reaction mechanism is assumed to account for the obtained results:

$$AC + S_2O_8{}^{2-} \xrightarrow{k} AC^+ + SO_4{}^{-\bullet} + SO_4{}^{2-} \qquad (7)$$

$$[Co(edta)]^{2-} + AC^+ \longrightarrow [Co(edta)]^- + AC \qquad (5)$$

$$[Co(edta)]^{2-} + SO_4{}^{-\bullet} \longrightarrow [Co(edta)]^- + SO_4{}^{2-} \qquad (8)$$

When the rate-determining step is reaction 7, while the successive reactions (Eqs. 5 and 8) are much faster, the rate equation is $-d[S_2O_8{}^{2-}]/dt=(1/2)d[[Co(edta)]^-]/dt=k[AC][S_2O_8{}^{2-}]$, being in agreement with the linear plots in Fig. 2.

The obtained results must represent a new type of oxidizing reagent in which the cation radical AC^+ serves as an electron-carrier. We believe that many types of oxidation reactions using AC^+ with $OH^{\bullet}$ and $SO_4{}^{-\bullet}$ radicals can be designed by using AC. The fact that the reaction rate of Eq. 7 is rather fast is interesting regarding practical use. Namely, the AC as an efficient catalyst may be used in place of the silver(I) ion for peroxodisulfate reactions. As far as the reaction mechanisms are concerned, it is comparable to the Fenton-reagent and the Haber–Weiss mechanism. The chain cycle of AC/AC^+ may be more useful than that of Fe^{2+}/Fe^{3+}, Ti^{3+}/Ti^{4+} etc. in the Fenton-like reagents which have been known up to now,[4] because AC/AC^+ is a solid-powder particle which is rather incapable of making complexes with most organic substances. The most important matter from the viewpoint of the catalysis of activated carbon would be the oxidizing ability of the AC^+ radical. As far as the oxidations of the oxalate ion and $[Co(edta)]^{2-}$ are concerned, it is noted that the AC/AC^+ cycle mentioned in this study is comparable to the $[Ru(bpy)_3]^{2+*}/[Ru(bpy)_3]^{3+}$ cycle in the photoinduced reactions in our previous studies.[6,7]

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