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Studies of the Anodic Oxidation of the Cyanide Ion in the Presence of the Copper Ion. III. Identification of the Reaction Intermediate by Means of ESR Spectroscopy

Seiji Yoshimura, Akira Katagiri,** Yasuo Deguchi,** and Shiro Yoshizawa*

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606

***Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University,*
Yoshida, Sakyo-ku, Kyoto 606

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The formation of the tetracyanocuprate(II) ion ($Cu(CN)_4^{2-}$), which was expected as a reaction intermediate in the anodic oxidation of the cyanide ion in the presence of the copper ion, has been investigated by means of ESR measurement. When a potassium cyanide solution containing a small amount of copper(I) cyanide was electrolyzed, an intermediate copper(II) species was found at the anode in the dissolved state. The ESR spectrum of the intermediate in the solidified state was obtained by freezing the solution in the resonant cavity. The intermediate was identified as $Cu(CN)_4^{2-}$ by a comparison of its spectrum to that of $Cu(CN)_4^{2-}$ already reported by other authors. When the ratio of the total copper(I) concentration to the total cyanide concentration in the solution was not too small, solid copper(II) cyanide was deposited on the anode during electrolysis.

In the investigation of the anodic oxidation of the cyanide ion, we have found a marked catalytic effect of the copper ion on this reaction.[1] We have postulated the formation of the tetracyanocuprate(II) ion ($Cu(CN)_4^{2-}$) as an intermediate in this catalytic electrochemical reaction, and have proposed the following mechanism, which is consistent with the results of several other electrochemical measurements:[2]

$$Cu^{I}(CN)_4^{3-} \longrightarrow Cu^{II}(CN)_4^{2-} + e^- \qquad (1)$$

$$Cu^{II}(CN)_4^{2-} + CN^- \longrightarrow Cu^{I}(CN)_4^{3-} + \frac{1}{2}(CN)_2 \qquad (2)$$

On the other hand, Longo and Buch[3] have studied the ESR and optical spectra of the unstable species produced in the chemical reaction between Cu^{II} and CN^-, and have identified the species as $Cu^{II}(CN)_4^{2-}$. The aim of the present paper is to confirm the formation of $Cu(CN)_4^{2-}$ in the anodic cyanide oxidation in the presence of the copper ion by means of ESR measurement.

Experimental

The ESR spectra were measured by the use of a JEOL JES-ME-3X spectrometer with X-band microwaves and with a field-moduration frequency of 100 kHz. A cylindrical resonant cavity of the TE_{011} mode was used. The temperature of the cavity was held constant by controlling the cold nitrogen-gas flow. In order to determine the g-values and hyperfine-coupling constants of the spectra, Mn^{2+} doped into MgO was used as the standard substance.

Two types of electrolysis cells, shown in Fig. 1, were used for the measurement of the ESR spectra during electrolysis. Both cells were made from a quartz tube (0.72 mmϕ in inner diameter) and were equipped with a platinum wire anode (0.4 mmϕ) coaxially. A platinum plate was used as the cathode. Cell (a) was set in the ESR spectrometer so that the anode was located at the center of the resonant cavity. By using this cell, the ESR spectrum of a paramagnetic substance, which was formed on the surface or in the vicinity of the anode, was measured. In the case of Cell (b) the platinum wire anode was located above the cavity, and the electrolyte was forced to flow downward. Thus, a paramagnetic substance, which was formed in the dissolved state, was detected. The temperature was kept constant at 25 °C in both cases. Electrolysis was performed at a constant current between 30 μA and 120 μA by means of a Hokuto Denko HA-104 galvanostat whose maximum output voltage was 50 V.

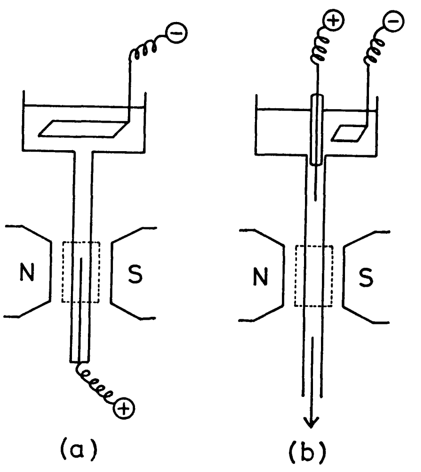

Fig. 1. Electrolysis cells for measurement of ESR absorption spectra at 25 °C.

For the purpose of measuring the ESR spectrum of a frozen solution, a polyethylene cell (2.5 mmϕ in inner diameter) was used. While a constant current was passed through at the platinum wire anode (0.4 mmϕ), the cell was brought into the cavity, whose temperature was held at −100 °C, whereby the electrolytic solution was frozen within a short time.

Electrolytic solutions were prepared from reagent-grade potassium cyanide and copper(I) cyanide. No supporting electrolyte was used, because the concentration of cyanide was sufficiently high. The compositions of the solutions were expressed in terms of the total cyanide concentration (C_{CN^-}) and the total copper(I) concentration ($C_{Cu(I)}$). C_{CN^-} and $C_{Cu(I)}$ were varied from 1.3 to 3.3 $mol \cdot dm^{-3}$, and from 0.1 to 0.3 $mol \cdot dm^{-3}$, respectively, while the $C_{Cu(I)}/C_{CN^-}$ ratio was varied from 1/3 to 1/33. Solid copper(II) cyanide was synthesized either by the chemical reaction of aqueous copper(II) sulfate with aqueous potassium cyanide[4] or by the anodic oxidation of copper in an aqueous potassium cyanide solution.[5]

Results

ESR Measurement during Electrolysis. When electrolysis was started in Cell(a) at a constant anodic current of 100 μA in a solution in which $C_{Cu(I)}$ and C_{CN^-} were 0.1 and 3.0 mol·dm^{-3} respectively, ESR absorption was observed immediately. Its intensity increased with the time at first, and then a steady state was reached. Figure 2 shows the ESR spectrum in the steady state. The spectrum shows four hyperfine lines which suggest the formation of a certain copper(II) species. The same spectrum was obtained in other experiments, where the current was 30, 60, or 120 μA, and where C_{CN^-} was 1.3, 2.3, or 3.3 mol·dm^{-3}, but $C_{Cu(I)}$ was constant at 0.1 mol·dm^{-3}. The steady-state intensity of the absorption was higher for the larger current, and for the higher concentration of the total cyanide, if the total copper(I) concentration was constant. When the current was switched off, the spectrum soon disappeared.

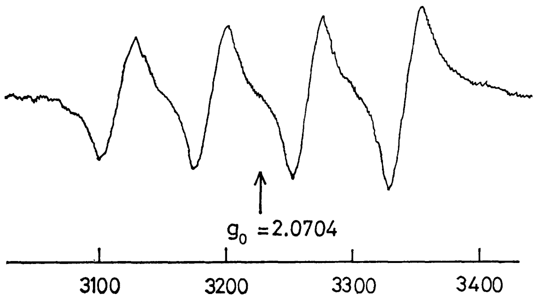

Fig. 2. ESR absorption spectrum during electrolysis at small $C_{Cu(I)}/C_{CN^-}$ ratio.
$C_{Cu(I)}$: 0.1 mol·dm^{-3}, C_{CN^-}: 3.0 mol·dm^{-3}, temp: 25 °C.

The same spectrum was observed when electrolysis was performed in a flowing solution in Cell(b), with the other conditions being the same. This indicates that the paramagnetic species was formed in the dissolved state in the solution.

Figure 3 shows the ESR spectrum measured with Cell (a) at a constant anodic current of 100 μA for the solution in which $C_{Cu(I)}$ and C_{CN^-} were 0.3 and 0.9 mol·dm^{-3} respectively. The same spectrum was obtained when the current was reduced to 50 μA and then further to 10 μA. The ESR absorption intensity increased continuously with the electrolysis time, and no steady state was reached. This spectrum agreed with that obtained independently for solid copper(II) cyanide.

ESR Measurement of the Reaction Intermediate in a Frozen Solution. Electrolysis was made in the polyethylene cell at a constant anodic current (100 μA) for a solution in which $C_{Cu(I)}$ and C_{CN^-} were 0.1 and 3.0 mol·dm^{-3} respectively. While the electrolysis was continued, the cell was inserted into the resonant cavity, held at a temperature of −100 °C, so that the anode was positioned at the center of the cavity. When the solution was frozen, the current became zero. Figure 4 shows the ESR spectrum of the frozen solution thus obtained. No change was observed in the spectrum so long as the sample was held in the frozen state.

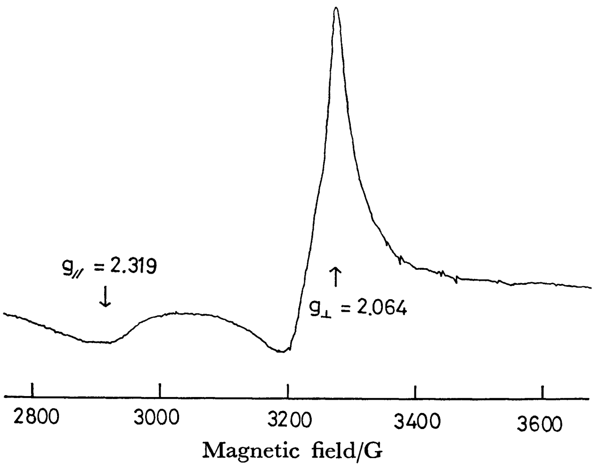

Fig. 3. ESR absorption spectrum during electrolysis at not too small $C_{Cu(I)}/C_{CN^-}$ ratio.
$C_{Cu(I)}$: 0.3 mol·dm^{-3}, C_{CN^-}: 0.9 mol·dm^{-3}, temp: 25 °C.

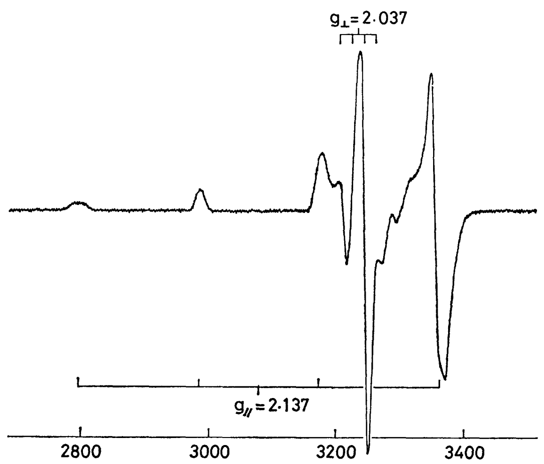

Fig. 4. ESR absorption spectrum of the frozen solution of small $C_{Cu(I)}/C_{CN^-}$ ratio.
$C_{Cu(I)}$: 0.1 mol·dm^{-3}, C_{CN^-}: 3.0 mol·dm^{-3}, temp: −100 °C.

Discussion

The ESR spectrum (Fig. 2) which was observed in the case of a small $C_{Cu(I)}/C_{CN^-}$ ratio exhibits an isotropic character. This is ascribed to a certain compound of divalent copper (^{65}Cu and ^{63}Cu) with nuclear spin $I=3/2$, because the spectrum has four absorption lines equally separated. Since the anisotropic terms of spin Hamiltonian are averaged out to zero for a solution spectrum, the positions of the absorption lines are determined only by isotropic terms. The isotropic g-facter, g_0, and the isotropic hyperfine-coupling constant. A_0, are obtained from Fig. 2 with reference to the standard Mn^{2+} sample; they are shown in the left-hand column of Table 1.

Table 1. ESR parameters of the intermediate investigated in this work and of $Cu^{II}(CN)_4^{2-}$

	The intermediate investigated in this work (Figs. 2 and 4)	$Cu^{II}(CN)_4^{2-}$ (Longo and Buch)
g_0	2.0704	2.071[a)]
$g_{//}$	2.137	2.146
$g_\perp$	2.037[a)]	2.033
$\lvert A_0\rvert\ (10^{-4}\ cm^{-1})$	71.4	81[a)]
$\lvert A_{//}\rvert\ (10^{-4}\ cm^{-1})$	188	190
$\lvert A_\perp\rvert\ (10^{-4}\ cm^{-1})$	13[a)]	27

a) Calculated by means of Eqs. 3 and 4.

The spectrum of the frozen solution (Fig. 4) shows the features of an axially symmetrical compound in a random orientation. The parallel and perpendicular components of the g-tensor, $g_{//}$ and $g_\perp$, and the parallel and perpendicular components of the hyperfine- coupling tensor, $A_{//}$ and $A_\perp$, are obtained from Fig. 4; they are shown in the left-hand column of Table 1. Thus, $g_{//}$ and $A_{//}$ are determined from the three low-field peaks on the spectrum. However, $g_\perp$ and $A_\perp$ are difficult to determine directly from the spectrum; therefore, they are calculated by the use of Eqs. 3 and 4,[6)] together with the values of g_0 and A_0:

$$g_0 = \frac{1}{3}(g_{//}+2g_\perp) \tag{3}$$

$$A_0 = \frac{1}{3}(A_{//}+2A_\perp) \tag{4}$$

It has been known for a long time that an unstable purple compound is formed in the reaction between cyanide and the copper(II) ion (Eq. 5):

$$Cu(II) + CN^- \longrightarrow Cu(I) + \frac{1}{2}(CN)_2 \tag{5}$$

Several authors have postulated the composition of this compound from the kinetics of the reaction.[7,8)] Longo and Buch[3)] conducted a reaction between copper(II) sulfate and potassium cyanide in methanol, dimethylformamide, and water at a low temperature. They measured the ESR spectra of the unstable purple compound in the liquid methanol solution and in the frozen solution in each solvent, the latter being obtained by freezing the reaction mixture quickly. They thus obtained spectra with an axially symmetrical character, and concluded the purple compound to be square-planar $Cu^{II}(CN)_4^{2-}$ from a consideration based on the crystal-field theory. The ESR parameters of the compound in an aqueous solution obtained by Longo and Buch are shown in the right-hand column of Table 1. Here, the values of g_0 and A_0 are calculated from Eqs. 3 and 4, because the spectrum of a liquid solution was not measured due to the instability of the compound in an aqueous solution. Taking account of the differences in the experimental conditions, the ESR parameters obtained by Longo and Buch and those in the present work are regarded as being in substantial agreement. It is, therefore, confirmed that $Cu^{II}(CN)_4^{2-}$ is formed as a reaction intermediate in the anodic oxidation of cyanide in the presence of the copper ion.

The spectrum (Fig. 3) which was observed during electrolysis in the solution with not too small a $C_{Cu(I)}/C_{CN^-}$ ratio exhibits an anisotropic character. No hyperfine structure can be seen because of the broad linewidth. From Fig. 3, $g_{//}$ and $g_\perp$ are found to be 2.319 and 2.064 respectively. The same spectrum was obtained for solid copper(II) cyanide. Therefore, it is concluded that solid copper(II) cyanide deposits on the anode during electrolysis under these conditions. This conclusion is consistent with the fact that the intensity of the ESR absorption grows continuously with the electrolysis time. The electrode potential, which was measured under the same conditions in the H-type cell,[2)] did not reach a steady value at any current, substantiating the above conclusion.

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