CHEMISTRY LETTERS, pp. 481 - 484, 1984.

IDENTIFICATION OF VARIOUS INTERMEDIATES IN THE REACTION OF CUPRIC IONS WITH CYANIDE IONS BY ESR SPECTROSCOPY. APPLICATION OF A NEW RAPID-FREEZING APPARATUS

Hiroshi YOKOI* and Akira HANAKI†
Chemical Research Institute of Non-aqueous Solutions, Tohoku University,
Katahira, Sendai 980
†National Institute of Radiological Sciences, Anagawa-4, Chiba 260

Various intermediates of mononuclear copper(II) cyanide complexes in the reaction of cupric ions with cyanide ions have been first identified by ESR spectroscopy after the use of a newly-constructed rapid-freezing apparatus. The formation of these intermediates has been found to depend primarily on the ratio $[CN^-]/[Cu^{2+}]$ and pH values. Possible structures of these intermediate complexes have been estimated by experiments with isotopes and by the application of the "rule of average environment" to their ESR parameters determined.

In aqueous solutions, cupric ions are rapidly reduced by cyanide ions to copper(I) cyanide complexes. Many authors have studied spectroscopically and electrochemically the kinetics and mechanism of this reaction,[1-3] and shown the formation of tetracyanocuprate ion, $[Cu(CN)_4]^{2-}$, as an important intermediate.[2,3] This tetracyanocuprate ion is almost the only intermediate copper(II) complex detected by ESR experiments.[3,4] In order to clarify the mechanism of the above reaction and to establish the coordination chemistry of cyanide, it is important to identify as many intermediates as possible in the reaction. The purpose of this paper is to report direct evidence for the formation of various copper(II) cyanide complexes as intermediates by the combined use of ESR and rapid-freezing of reaction mixtures.

For the above purpose, we constructed a new type of rapid-freezing apparatus used for rapid quenching of reactions (Fig. 1). This apparatus is adapted from earlier designs[5] with an important modification of the freezing method; the solutions coming out of jets are rapidly frozen as thin films on the whole inner surface of a copper cylinder cooled at about -200 °C. The syringe plungers and the mixer-nozzle assembly are synchronously driven by stepping motors under controlled speeds. The performance of this apparatus was totally tested on a ligand-exchange reaction of triethylenetetramine (trien) with $Cu\text{-}EDTA^{2-}$ as a model reaction, where rate = k_{obsd} $[trien]_{total}$ $[Cu\text{-}EDTA^{2-}]$ and $k_{obsd} = 4.5 \times 10^4\ M^{-1}s^{-1}$ (pH 9.0; 25 °C; 0.1 M $NaClO_4$).[6] The chemical quenching time of this apparatus under a specific experimental condition can be calculated from the concentration ratio $[Cu\text{-}trien^{2+}]/[Cu\text{-}EDTA^{2-}]$ in the frozen solution. The ESR spectra of $Cu\text{-}trien^{2+}$ and $Cu\text{-}EDTA^{2-}$ do not overlap at the $I_{Cu} = -3/2$ hyperfine lines of $g_{\parallel}$, and, accordingly, the above concentration ratio can be adequately approximated by the ratio of inte-

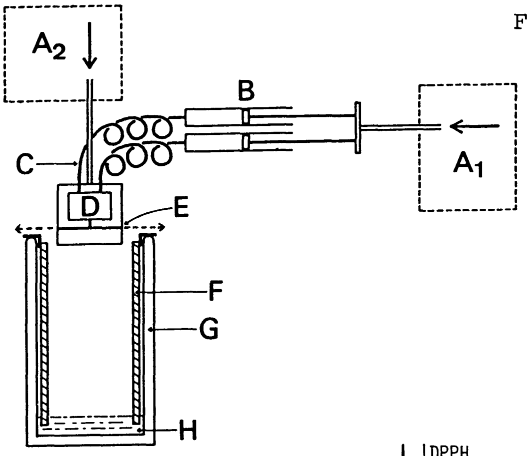

Fig. 1. Schematic illustration of a rapid-freezing apparatus used for rapid chemical quenching: A_1, stepping motor and driving assembly (the syringe plungers are driven as shown by the arrow); A_2, stepping motor and driving assembly (synchronized with A_1); B, syringes; C, teflon tubing; D, 8-jet mixer; E, nozzles (dotted lines, jets of solutions); F, copper cylinder (3.0 mm thickness); G, Dewar vessel; H, liquid nitrogen.

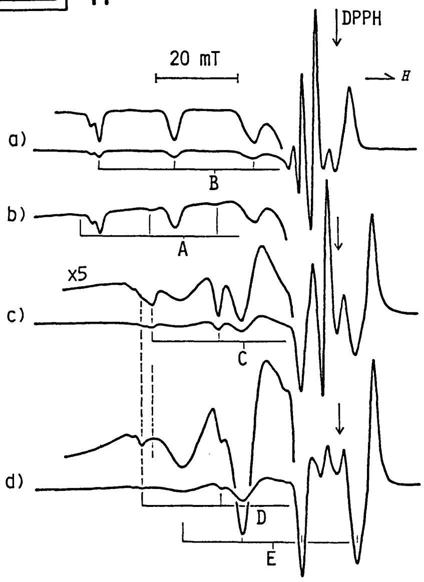

Fig. 2. ESR spectra of frozen solutions prepared by the rapid-freezing apparatus for reaction mixtures at pH 10.2: a) $R = 1$; b) $R = 3$; c) $R = 5$; d) $R \geq 7$ (as to A, B, C, *etc.*, see text).

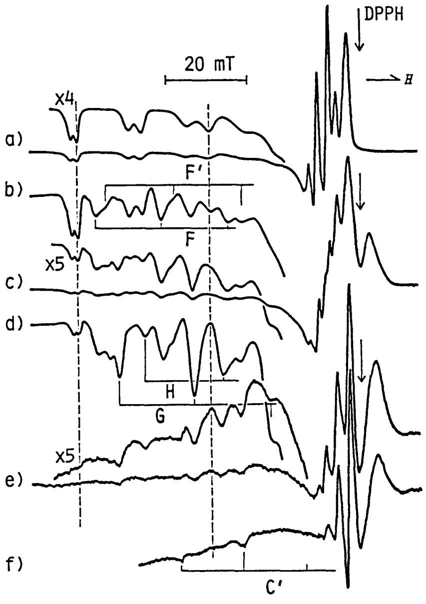

Fig. 3. ESR spectra of frozen solutions prepared by the rapid-freezing apparatus for reaction mixtures at pH 5.8: a) $R = 0$; b) $R = 1$; c) $R = 3$; d) $R = 5$; e) $R = 8$; f) $R = 12$.

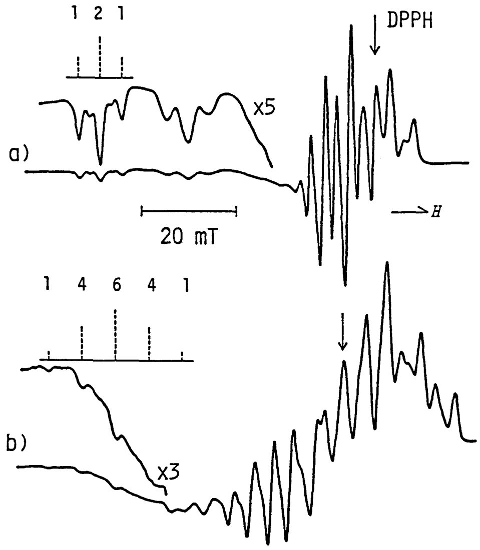

Fig. 4. ESR spectra of frozen solutions prepared by the rapid-freezing apparatus for reaction mixtures of $^{63}Cu^{2+}$ and $^{13}CN^-$ ions at pH 10.2: a) $R = 1$; b) $R = 8$. ^{13}C hyperfine structures of coordinated $^{13}CN^-$ ions are shown in both spectra, and some analyses of them at the $I_{Cu} = -3/2$ hyperfine lines of $g_\parallel$ are also exhibited by stick diagrams.

grated intensities of the hyperfine lines. The sample thin ice produced on the inner surface of the copper cylinder is collected and transferred to the finger part of an insertion-type liquid nitrogen Dewar vessel for X-band ESR spectrometers together with liquid nitrogen, and, then, ESR spectra are recorded at 77 K without hurry. Using the above model reaction, we could determine the minimum quenching time of 2.9 ± 0.4 ms for this rapid-freezing apparatus.

In this work, experiments were performed under the same operating condition of the apparatus as in the above minimum quenching time and under the following conditions of solutions; $[Cu^{2+}] = 1.25 \times 10^{-3}$ M, $[NaClO_4] = 0.20$ M, and varying R values, where $R = [CN^-]/[Cu^{2+}]$; the CN^- solutions were buffered at pH 10.2, 9.0, and 5.8 (0.05 M borate or 0.1 M acetate). Unstable mononuclear copper(II) cyanide complexes trapped by rapid-freezing were identified on the basis of both ESR parameters of $g_{\parallel}$ and $A_{\parallel}$, and they are lettered A, B, C, *etc.*, respectively.

Under alkaline conditions, no ESR signals are observed at $R = 0$, owing to the formation of $Cu(OH)_2$. As R increases from 1 to 15, the complex species of B, A, C, and D and E are formed successively at pH 10.2, as shown in Fig. 2; some of their ESR spectra are simultaneously observed overlapping each other, and the R dependence of the formation of these species are somewhat affected by pH values. The spectrum (d) in Fig. 2 is the same as the "anomalous spectrum" called by Long and Buch.4) We interpreted this spectrum as due to two different species, D and E, where the spectrum of D normally has an axial or nearly axial type of ESR line shape and the spectrum of E unusually has a nearly isotropic type. This interpretation was supported by Q-band ESR measurements and by experiments with the isotopes of ^{63}Cu and $^{13}CN^-$. Some results obtained by these isotope experiments at pH 10.2 are shown in Fig. 4. The spectra (a) in Figs. 2 and 4 are the same, except for extra ^{13}C hyperfine structures in the latter spectrum, in which the $g_{\parallel}$ hyperfine lines split into three lines with relative intensities 1:2:1. This fact indicates that these (a) spectra are due to a copper(II) complex with two equivalent CN^- ions. On the other hand, the spectrum (b) in Fig. 4, which corresponds to the "anomalous spectrum" with extra ^{13}C hyperfine structures, is composed of two overlapping spectra, as mentioned above. One is the spectrum of D with extra well-resolved ^{13}C hyperfine structures and the smallest $g_{\parallel}$ value in this study, where the $I_{Cu} = -3/2$ hyperfine line of $g_{\parallel}$ splits into five lines with relative intensities 1:4:6:4:1, indicating that D is a planar complex of $[Cu(CN)_4]^{2-}$. The other is a broad single line spectrum, which probably results from the addition of widespread ^{13}C hyperfine structures to the spectrum of E in Fig. 2. It is noteworthy that ESR signal intensities are remarkably weakened at $R = 3$ or 4, suggesting that copper(II) cyanide complexes formed at these R values may rapidly decompose to copper(I) complexes, in conformity with the previous prediction.3)

In acidic solutions at pH 5.8, F and F′, G, H, and C′ are formed successively, as R increases, as shown in Fig. 3; at $R > 6$, ESR signal intensities become remarkably weak. Judging from $g_{\parallel}$ and $A_{\parallel}$ values, G and C′ are obviously analogous in structure to B and C, respectively. In general, the "rule of average environment" holds good not only for visible absorption spectra of metal complexes,7) but also for ESR parameters of copper(II) complexes,8) as also exemplified here by the fact that the $g_{\parallel}$ values of $Cu(CN)_4^{2-}$, $Cu(CN)_2$, and Cu^{2+} increase in this order, as shown in Table 1. According to this rule, F and F′ are reasonably identified as copper-

(II) complexes with one CN^- ion, and H is considered as a complex with three CN^- ions. On referring also to R, C and C′ may possibly be complexes with four CN^- ions, which are of a different type to D.

All the results obtained here are summarized in Table 1.

Table 1. ESR Data and Possible Structures of Intermediate Copper(II) Cyanide Complexes

pH	$g_{\parallel}$	$\lvert A_{\parallel}\rvert$ cm^{-1}	Complex (ESR spectrum)	Possible structure[b)]	Remarks
9 – 10	2.256	0.0176	A	$Cu(CN)X$; X = OH^- or H_2O	analogous to F′
	2.209	0.0195	B	$Cu(CN)_2X$; X = OH^- or H_2O	analogous to G
	2.142	0.0163	C	$Cu(CN)_4$	analogous to C′
	2.129	0.0194	D	$Cu(CN)_4$; square planar	
			E	$Cu(CN)_4$; tetrahedral	g_0 = 2.09; $\lvert A_0\rvert$ = 0.013 cm^{-1}
5.8[a)]	2.287	0.0174	F	$Cu(CN)X$; X = $CH_3CO_2^-$ or H_2O	
	2.258	0.0177	F′	$Cu(CN)X_2$; X = $CH_3CO_2^-$ or H_2O	
	2.220	0.0192	G	$Cu(CN)_2$	
	2.168	0.0191	H	$Cu(CN)_3$	
	2.147	0.0155	C′	$Cu(CN)_4$	

a) In the case of R = 0 (Fig. 3a), cupric ions in acetate buffers are in two different states of acetate coordination with the ESR parameters: $g_{\parallel}$ = 2.360, $\lvert A_{\parallel}\rvert$ = 0.0158 cm^{-1}; $g_{\parallel}$ = 2.325, $\lvert A_{\parallel}\rvert$ = 0.0182 cm^{-1} (cf. $g_{\parallel}$ = 2.400, $\lvert A_{\parallel}\rvert$ = 0.0128 cm^{-1} for hydrated Cu^{2+} ions).

b) The structures are expressed with charge and coordinated water molecules omitted. All the complexes are essentially 4-coordinated planar ones. The coordination bond of OH^- is stronger than that of H_2O.

References

1) F. R. Duke and W. G. Courtney, *J. Phys. Chem.*, 56, 19 (1952); J. H. Baxendale and D. T. Westcott, *J. Chem. Soc.*, 1959, 2347.
2) R. Paterson and J. Bjerrum, *Acta Chem. Scand.*, 19, 729 (1965); O. Mønsted and J. Bjerrum, *ibid.*, 21, 1116 (1967); G. Nord and H. Matthes, *ibid.*, A28, 13 (1974).
3) S. Yoshimura, A. Katagiri, Y. Deguchi, and S. Yoshizawa, *Bull. Chem. Soc. Jpn.*, 53, 2434, 2437 (1980).
4) A. Long and T. Buch, *Inorg. Chem.*, 6, 556 (1967).
5) R. C. Bray, *Biochem. J.*, 81, 194 (1961); R. C. Bray, D. J. Lowe, C. Capeillere-Blandin, and E. M. Fielden, *Biochem. Soc. Trans.*, 1973, 1067; D. P. Ballou and G. A. Palmer, *Anal. Chem.*, 46, 1248 (1974); R. C. Bray, G. Palmer, and H. Beinert, *J. Biol. Chem.*, 238, 2667 (1964).
6) J. D. Carr, R. A. Libby, and D. W. Margerum, *Inorg. Chem.*, 6, 1083 (1967).
7) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York (1962), p. 107.
8) H. Yokoi, M. Otagiri, and T. Isobe, *Bull. Chem. Soc. Jpn.*, 44, 2395 (1971); H. Yokoi and A. W. Addison, *Inorg. Chem.*, 16, 1341 (1977).

(Received December 10, 1983)