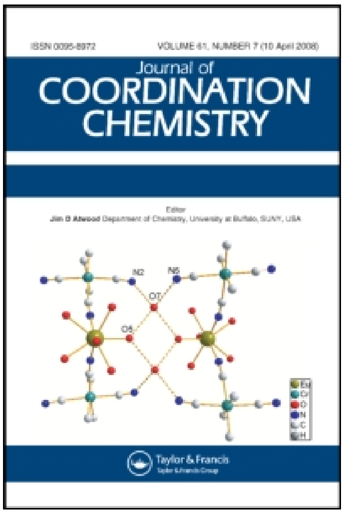

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NOTE

THE OXIDATION OF CYANIDE ION BY SILVER(III) IN ALKALINE MEDIA

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INTRODUCTION

Cyanide is a very important reagent in the electroplating industry, but is highly toxic. Detoxification of cyanide by oxidation has long been studied in connection with waste water treatment, which employs ozone,[1] hypochlorite and/or chlorine[2,3] as oxidants. The oxidation converts the highly toxic cyanide into non-toxic cyanate which readily hydrolyzes to ammonium ion and carbon dioxide in acidic media.[4] Recently, we undertook the study of the oxidation of iodide[5] and thiocyanate[6] by the tetrahydroxoargentate(III) ion in strongly alkaline media. Here, we wish to report the oxidation of cyanide under similar conditions. In fact, it is the study of thiocyanate oxidation that initiated our interest in the cyanide system, since cyanide is a hydrolysis product of potential thiocyanate oxidation intermediates.

EXPERIMENTAL

All stock solutions were made in doubly distilled water. Sodium hydroxide solutions were prepared from 50% low carbonate NaOH (Fisher). For $NaClO_4$ solutions, NaOH was neutralized with $HClO_4$ (Fisher), adjusted to pH 7 and filtered.[6] Cyanide solutions wre made daily by dissolving accurately weighed reagent grade NaCN (Fisher) in NaOH or $NaClO_4$ or a mixture of the two at ionic strength 1.2 M. Jackson's modification of Nessler's reagent was used to test for ammonia[7] which is a hydrolysis product of cyanate. $Ag(OH)_4^-$ solutions were prepared by electrolysis of silver foil (Handy and Harman) in 1.2 M NaOH solution as previously described.[8,9]

The kinetics of the reaction were studied at 25°C and 1.2 M ionic strength by the stopped-flow method. The reduction of $Ag(OH)_4^-$ was followed spectrophotometrically at its absorbance maximum of 267 nm. A large excess of cyanide was used throughout, and the reaction was found to be *pseudo*-first-order in $[Ag(OH)_4^-]$. The reaction stoichiometry at excess $Ag(OH)_4^-$ was determined from the final Ag(III) absorbance after mixing in the stopped-flow apparatus.

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RESULTS AND DISCUSSION

Adding Nessler's reagent directly to the reaction mixture proved negative for NH_3 even with excess silver(III). However, when the reaction mixture was acidified with 6 M HCl to pH 3–4, then brought back to $[OH^-] = 1.2$ M with 6 M NaOH, addition of Nessler's reagent turned the solution to reddish-brown, revealing the presence of ammonia. This indicates that ammonia was produced from the acidification of the reaction mixture, but not from the oxidation of cyanide. Thus, we conclude that the oxidation product is cyanate ion. In acidic media, cyanate hydrolyzes to carbon dioxide and ammonium ion as in (*1*).[10]

$$OCN^- + 2H^+ + H_2O \rightarrow CO_2 + NH_4^+ \qquad (1)$$

With excess cyanide, the reddish-brown colour formed (after hydrolysis), but disappeared upon shaking, probably due to the complexation, by CN^-, of Hg^{2+} in the Nessler's reagent. In fact, when excess Nessler's reagent was added, the characteristic reddish-brown colour did persist.

The stoichiometry results with excess $Ag(OH)_4^-$ are listed in Table I. Ratios of $\Delta[CN]/\Delta[Ag(III)]$ close to 2 were obtained. The 2:1 stoichiometry is consistent with a 2-electron oxidation to cyanate accompanied by formation of AgCN.

$$Ag(OH)_4^- + 2CN^- \rightarrow AgCN + OCN^- + H_2O + 2OH^- \qquad (2)$$

The reaction mixture was slightly milky due to AgCN and then turned cloudy with a black precipitate from the decomposition of excess $Ag(OH)_4^-$. With excess cyanide, no precipitate was observed. The clear solution indicated that all Ag(I) formed $Ag(OH)_2^-$ and /or the $Ag(CN)_2^-$ complex ($\beta_2 = 1.26 \times 10^{22}$).[11] At very high $[CN^-]$, the ratio should approach a value of 3 according to the following reaction.

$$Ag(OH)_4^- + 3CN^- \rightarrow Ag(CN)_2^- + OCN^- + H_2O + 2OH^- \qquad (3)$$

The kinetic experiments were carried out at 25°C and 1.2 M ionic strength with initial [Ag(III)] generally between 2×10^{-5} and 5×10^{-5} M, and a large excess of cyanide. The reaction is *pseudo*-first-order in $[Ag(OH)_4^-]$ for at least four half-lives. The observed rate constant, k_{obsd}, is independent of $[OH^-]$ (Table II) and proportional to $[CN^-]$ with intercept close to zero as shown in Figure 1, thus leading to the second-order rate constant, $k = (7.7 \pm 0.3) \times 10^2\ M^{-1}\,s^{-1}$.

As in other low spin d^8 complexes, the square-planar geometry of $Ag(OH)_4^-$ leaves the axial sites open for nucleophilic attack. Thus, $Ag(OH)_4^-$ reactions typically begin with axial attack at Ag(III) and the formation of five-coordinate transients[12–14].

TABLE I
Stoichiometry of the cyanide oxidation with excess Ag(III) ($\mu = 1.2$ M, T = 25°C).

$10^4[Ag(III)]_0$, M	$10^4[CN^-]_0$, M	$10^4[Ag(III)]_\infty$	$\Delta[CN^-]/\Delta[Ag(III)]$
2.42	0.5	2.14	1.8
3.02	1.0	2.55	2.3
3.13	1.5	2.38	2.0
3.09	2.5	2.01	2.3
		Average	2.1 ± 0.2

TABLE II

Pseudo-first-order rate constants for cyanide oxidation ($\mu = 1.2$ M, T = 25°C).

$10^3[CN^-]$, M	$[OH^-]$, M	k_{obsd}, s^{-1}	k_{calc}, s^{-1}
1.0	0.6	1.14	0.96
2.5	0.6	1.96	2.12
5.0	0.6	4.13	4.04
7.5	0.6	5.63	5.95
10.0	0.6	8.09	7.87
5.0	0.12	4.05	4.04
5.0	0.3	4.11	4.04
5.0	0.9	3.98	4.04
5.0	1.2	4.09	4.04

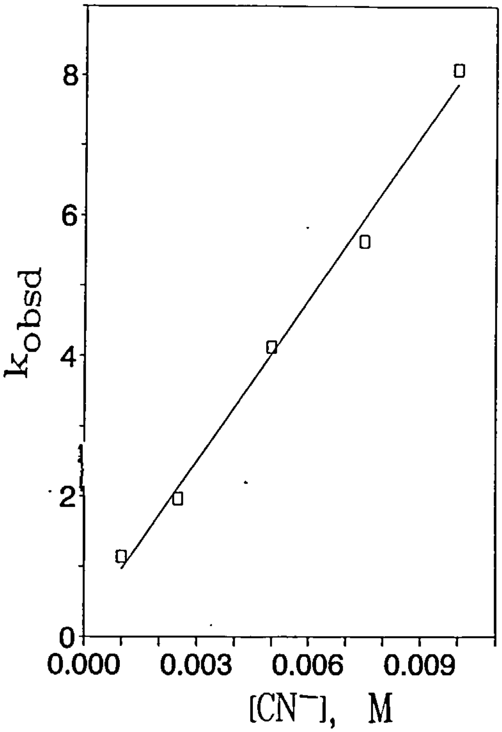

FIGURE 1 Dependence of k_{obsd} on cyanide concentration at 25°C, $[OH^-] = 0.6$ M and $\mu = 1.2$ M. The solid line is from a least-squares treatment.

Redox may occur either with or without subsequent ligand replacement. The two-electron transfer is accomplished either in a single step, like the sulfite,[8] thiocyanate,[6] iodide[5] and thiosulfate[13] reactions or in two consecutive steps with Ag(II) intermediates, as in the oxidations of HO_2^-,[14] $Mn(CN)_6^{4-}$, $W(CN)_8^{4-}Fe(CN)_6^{3-}$ and MnO_4^-,[15] and *tert*-butylphenolate ion.[16]

There are three possible redox mechanisms consistent with the simple kinetics of the cyanide oxidation: (*i*) direct one-step, two-electron transfer from CN^- to Ag(III), forming CN^+ which reacts rapidly with free OH^-;

$$Ag(OH)_4^- + CN^- \rightarrow Ag(OH)_2^- + CN^+ + 2OH^- \rightarrow Ag(OH)_2^- + OCN^- + H_2O \quad (4)$$

(*ii*) sequential one-electron transfers, in which one electron is transferred from CN^- to $Ag(OH)_4^-$, forming a Ag(II) intermediate as well as $CN^{\cdot}$ and/or $(CN)_2^{\cdot -}$ radicals;[17] the radicals may react with $Ag(OH)_4^-$ or the Ag(II) intermediate to give cyanogen which hydrolyzes to cyanate ion in alkaline media; (*iii*) one-step oxygen-atom transfer, as in the case of cyanide oxidation by permanganate[18] and hypochlorite[19] and the oxidations of nonmetal oxoanions[9,12] by $Ag(OH)_4^-$ (in which cyclic intermediates are formed). By this mechanism, CN^- would attack the coordinate hydroxyl on the $Ag(OH)_4^-$ and become loosely bonded to the oxygen. The bonding weakens the O–Ag bond of $Ag(OH)_4^-$ (the O–Mn bond in the case of permanganate and O–Cl bond in hypochlorite) and finally frees the oxygen.

Because of the instability of Ag(II), the stoichiometry with excess silver (Table I) seems inconsistent with (*ii*).[14] The linear geometry of bound $-CN^-$ and OCN^- makes (*iii*) unlikely. Thus, we prefer case (*i*), which is also supported by the similarity of iodide, thiocyanate and cyanide, both in their oxidation kinetics and chemical properties. While it is certainly possible that carbon–oxygen formation occurs within the five-coordinate intermediate (*i.e.* without separation of CN^+), this is not required by the kinetics as is the case in some other Ag(III) systems.[14,20] Similarly, the hydroxide-independence of the rate constants is an indication that there is no OH^- replacement prior to the redox reaction.

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REFERENCES

1. G. Ionescu, F. Matei and A. Duca, *Rev. Chim.*, **34**, 810 (1983).
2. E.B. Besselivre, *The Treatment of Industrial Wastes* (McGraw-Hill, New York, 1969).
3. B. Kozcorowski and J. Kucharzki, *Industrial Waste Disposal* (Pergamon, New York, 1972), 1st English Edition.
4. M.B. Jensen, *Acta Chem. Scand.*, **12**, 1657 (1958).
5. I. Kouadio, L.J. Kirschenbaum and R.J. Mehrotra, *J. Chem. Soc., Dalton Trans.*, 1929 (1990).
6. L.J. Kirschenbaum and Y. Sun, *Inorg. Chem.*, **30**, 2360 (1991).
7. F.D. Snell and C.T. Snell, *Colorimetric Methods of Analysis*, V2, 3rd Ed. (D. van Nostrand Company, Inc., Toronto, 1949), p. 814.
8. L.J. Kirschenbaum, J.H. Ambrus and G. Atkinson, *Inorg. Chem.*, **12**, 2832 (1973).
9. L.J. Kirschenbaum, I. Kouadio and E. Mentasti, *Polyhedron*, **8**, 1299 (1990).
10. R.G.R. Bacon and R.S. Irwin, *J. Chem. Soc.*, 778 (1958).
11. L.G. Sillén and A.E. Martell (Eds.), *Stability Constants* (The Chemical Society, London, 1964), p. 110.

12. R.N. Mehrotra and L.J. Kirschenbaum, *Inorg. Chem.*, **28**, 4327 (1989).
13. J.D. Rush and L.J. Kirschenbaum, *Inorg. Chem.*, **24**, 744 (1985).
14. E.T. Borish and L.J. Kirschenbaum, *J. Chem. Soc., Dalton Trans.*, 749 (1983).
15. (a) E.T. Borish, L.J. Kirschenbaum and E. Mentasti, *J. Chem. Soc., Dalton Trans.*, 1789 (1985); (b) L.J. Kirschenbaum, E.T. Borish and J.D. Rush, *Israel J. Chem.*, **25**, 159 (1985).
16. R.K. Panda and L.J. Kirschenbaum, *J. Chem. Soc., Dalton Trans.*, 217 (1989).
17. A.W. Adamson, *J. Phys. Chem.*, **56**, 858 (1952).
18. R. Stewart and R. Van der Linden, *Can. J. Chem.*, **38**, 2237 (1960).
19. G.E. Mapstone and B.R. Thorn, *J. Appl. Chem. Biotechnol.*, **28**, 135 (1978).
20. L.J. Kirschenbaum and R.K. Panda, *Polyhedron*, **7**, 2753 (1988).