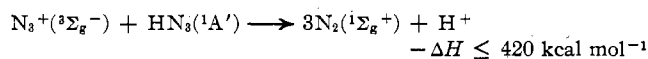
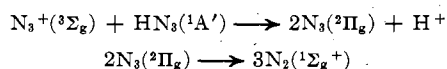


complexes²) or several orders of magnitude, we are unable to determine the relative values of k_{-3} and k_4 from the experimental value of B .

Although step IV is very highly exothermic, the ground-state reaction³³



is forbidden by spin-correlation rules. Step IV thus proceeds either (a) from the lowest singlet of N_3^+ or (b) *via* the sequence



(33) (a) The term state for N_3^+ is given in ref 30. From electron impact data, these authors give ΔH_f as $\leq 388 \text{ kcal mol}^{-1}$, but in solution ΔH_f should be substantially smaller. (b) B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959), gave $61.9 \text{ kcal mol}^{-1}$ as the heat of formation of undissociated HN_3 at infinite dilution. Dissociation into $\text{H}^+ + \text{N}_3^-$ requires $3.6 \text{ kcal mol}^{-1}$. $\Delta H_f(\text{N}_3^-) = 35 \pm 1 \text{ kcal mol}^{-1}$.

with the second process involving azide radicals of opposite spin. Either the N_3^+ triplet state or the neutral N_3 radical would be expected to be responsible for initiating the polymerization of acrylonitrile. Finally, it should be noted that the isotopic distribution of the nitrogen formed in the present system would be expected to be the same as that found in studies involving ^{15}N - ^{15}N azide radical species.^{7,34}

Acknowledgment.—This investigation was supported in part by Public Health Service Research Grant GM-08893-07 from the National Institute of General Medical Sciences, Public Health Service, and in part by National Science Foundation Grant GP-4277. L. J. K. acknowledges, with gratitude, the receipt of an NSF cooperative fellowship and a NASA traineeship.

(34) K. Clusis and H. Schumacher, *Helv. Chim. Acta*, **41**, 972 (1958).

CONTRIBUTION FROM THE J. HEYROVSKÝ INSTITUTE OF POLAROGRAPHY, CZECHOSLOVAK ACADEMY OF SCIENCES, PRAGUE, CZECHOSLOVAKIA

Redox Reactions of Cobalt-Cyanide Complexes. III.¹ Reaction of $\text{Co}(\text{CN})_5\text{H}^{3-}$ with *p*-Benzoquinone

BY J. HANZLÍK AND A. A. VLČEK

Received July 23, 1968

p-Benzoquinone reacts in alkaline solutions with $\text{Co}(\text{CN})_5\text{H}^{3-}$ *via* two paths: a slow, pH-independent, direct reaction with the hydride species ($k_1 = 13.5 \text{ M}^{-1} \text{ sec}^{-1}$) and a fast reaction with the univalent cobalt complex $\text{Co}(\text{CN})_5^{4-}$, formed by the deprotonation of the hydride. The rate constant for the reaction with $\text{Co}(\text{CN})_5^{4-}$ is of the order $10^9 \text{ M}^{-1} \text{ sec}^{-1}$. In both cases $(\text{CN})_5\text{CoOC}_6\text{H}_4\text{OH}^{2-}$ is the only primary product of the reaction. The formal rate constant of the process at $\text{pH} > 9.2$ and 0° is $k = 13.5 + 8.7 \times 10^4[\text{OH}^-]$. An addition mechanism is proposed for both reaction paths, the direct hydride transfer or an insertion process being excluded. At $\text{pH} < 9$, *p*-benzoquinone is partly reduced in two one-electron steps, $(\text{CN})_5\text{Co}(\mu\text{-OC}_6\text{H}_4\text{O})\text{Co}(\text{CN})_5$ being the primary product of this reaction path.

In the preceding paper of this series¹ the reaction of pentacyanocobaltate(II) with *p*-benzoquinone was shown to proceed *via* the redox addition mechanism under the formation of a bridge species, $(\text{CN})_5\text{Co}(\mu\text{-OC}_6\text{H}_4\text{O})\text{Co}(\text{CN})_5^{6-}$ (I). I decomposes giving in the first step $(\text{CN})_5\text{CoOC}_6\text{H}_4\text{OH}^{3-}$ (II) and $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$.

p-Benzoquinone is known to react also with the hydrogenated solutions of pentacyanocobaltate;² the reaction shows, however, several peculiar features, most probably due to the rather complicated system in which the reaction was studied. In the present paper we wish to report our results on the kinetics and mechanism of the reaction of *p*-benzoquinone with $\text{Co}(\text{CN})_5\text{H}^{3-}$ in the absence of hydrogen.³ As $\text{Co}(\text{CN})_5\text{H}^{3-}$,

unlike $\text{Co}(\text{CN})_5^{3-}$, is not able to react by an ordinary redox addition mechanism, it was of importance to compare the mechanism of the redox reaction of these two complexes with the same substrate and to compare the intermediates and products of the reactions in order to find out what species represents the reactant proper in the reduced pentacyanocobaltate(II) solutions. Furthermore, as $\text{Co}(\text{CN})_5\text{H}^{3-}$ is formally a two-electron agent, it was hoped that its reaction with *p*-benzoquinone might result in the direct formation of II which could thus have been prepared in the pure form.

Experimental Section

Most of the experimental details were the same as described in our earlier paper.¹ The spectrophotometric measurements were carried out using a Unicam SP 800 spectrophotometer:

(3) No molecular hydrogen was introduced into the system. There might, however, have been hydrogen present owing to the partial decomposition of the hydride species; see Experimental Section.

(1) Part II: A. A. Vlček and J. Hanzlík, *Inorg. Chem.*, **6**, 2053 (1967).

(2) J. Kwiatek, I. L. Mador, and J. K. Seyler, *J. Am. Chem. Soc.*, **84**, 304 (1962); *Advances in Chemistry Series*, No. 87, American Chemical Society, Washington, D. C., 1963, p 201.

Preparation of the Solutions of $\text{Co}(\text{CN})_5\text{H}^{3-}$.—Solutions of $\text{Co}(\text{CN})_5\text{H}^{3-}$ were prepared from the aqueous solutions of pentacyanocobaltate(II) by the reduction with sodium borohydride or molecular hydrogen or electrolytically from aqueous solutions of $\text{Co}(\text{CN})_5\text{Br}^{3-}$. The procedure was in all cases controlled polarographically. In accordance with previous findings⁴ and contrary to the statement of Simándi and Nagy,⁵ it was confirmed that, in aqueous solution, the product of the reduction of pentacyanocobaltate(II) by any of the three methods is an *electroinactive* species identical with that described as $\text{Co}(\text{CN})_5\text{H}^{3-}$. Electrolytical reduction has been chosen as the most convenient one, since there is, therefore, no other reducing agent present in the solution, and the reduction can be carried to completion (*i.e.*, to complete disappearance of all $\text{Co}(\text{CN})_5^{2-}$ from the solution), at least at cobalt concentrations below *ca.* $4 \times 10^{-3} M$, used in our experiments. The solutions thus obtained were sufficiently stable.

The electrolysis was carried out in the cell depicted in Figure 1, which made it possible to follow the reaction without any transfer of the solution after electrolysis. A mercury pool cathode (12 cm^2) was used the potential of which was kept constant by a potentiostat at -1.5 V against a silver-silver chloride electrode in saturated KCl solution (*sae*). The electrolyzed solution contained the necessary buffered system and potassium chloride to keep the pH and ionic strength constant. The procedure took place in argon atmosphere at 0° . The complete electrolysis, with transport accelerated by a magnetic stirrer, took place for 25 ml of a $2 \times 10^{-3} M$ solution in 15–20 min.

Kinetic Measurements.—After the completion of the electrolysis, the necessary amount of *p*-benzoquinone solution was introduced by a syringe through the opening P into the cell. The subsequent reaction was followed polarographically by determining the concentration of the unreacted quinone as well as of the products formed. All of the kinetic measurements were carried out at 0° . The time necessary for introducing the second reactant and complete mixing of the solution was less than 10 sec.

Results

Stoichiometry and Products of the Reaction.—The addition of *p*-benzoquinone in a substoichiometric concentration to a solution of $\text{Co}(\text{CN})_5\text{H}^{3-}$ results, in alkaline solution (borate buffer, pH 10.2, $\mu = 0.5 M$, 20°), in an immediate formation of a weak brown-yellow color, and the polarogram shows one reduction wave at -1.3 V (against *sae*) and one oxidation wave at $+0.02 \text{ V}$ (against *sae*). These waves are identical with those of II in the same solution.¹ The height of these waves is directly proportional to the concentration of *p*-benzoquinone up to the point at which $[p\text{-benzoquinone}] = [\text{Co}(\text{CN})_5\text{H}^{3-}]$. Further additions of *p*-benzoquinone result in the appearance of its reduction wave at -0.05 V (*sae*), the waves due to II being constant. After prolonged standing of the solution, the appearance of $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$ and hydroquinone is detected. This process corresponds to the decomposition of II described previously.¹

From this it follows that in alkaline solution 1 mol of $\text{Co}(\text{CN})_5\text{H}^{3-}$ reacts with 1 mol of *p*-benzoquinone, the species $(\text{CN})_5\text{CoOC}_6\text{H}_4\text{OH}^{3-}$ being the only product of the reaction. This result has been confirmed also spectrophotometrically.

In weakly alkaline solutions (pH < 9) the same

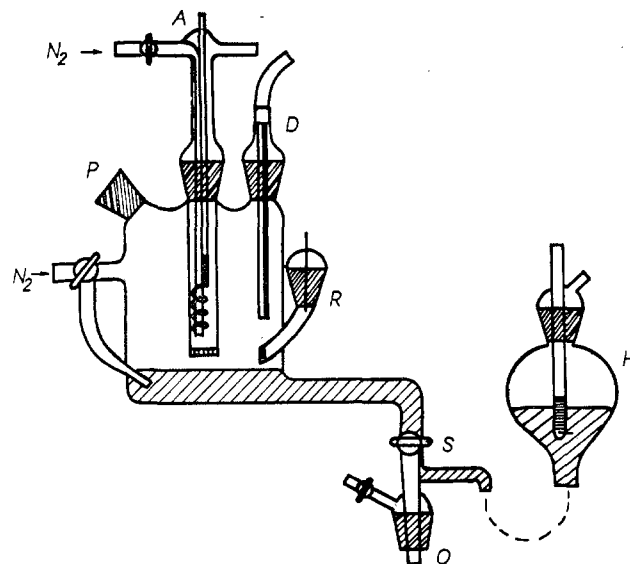


Figure 1.—Cell for the electrolytic preparation of $\text{Co}(\text{CN})_5\text{H}^{3-}$: H, mercury reservoir for the working cathode C; A, anode; R, reference electrode; D, dropping mercury electrode; P, connection for introducing solution into the cell; O, outlet of the reduced solution; S, three-way stopcock.

process results in the formation of II also. However, spectrophotometric as well as polarographic data reveal the formation of the bridge species I, which under these conditions decomposes rather rapidly giving II and $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$.¹ The presence of $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$ is seen polarographically from the first stages of the reaction, its concentration being *much higher than that corresponding to the decomposition of II* under the same conditions. The final product of the reaction under these conditions contains a mixture of II and $\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}$ in the ratio $\sim 3:2$ (pH 8.4, $1 M \text{ KCl}$, 20° , reaction time 5–15 min).

From these results it can be concluded that in weakly alkaline solutions the reaction studied proceeds by two paths, one leading to the direct formation of species II and the second one, to the primary formation of bridge species I. The contribution of the second path increases with decreasing pH.

Kinetics of the Reaction.—At 0° the reaction between *p*-benzoquinone and $\text{Co}(\text{CN})_5\text{H}^{3-}$ proceeds with such a rate that it can be followed by conventional polarographic technique.

The two reactants being taken at equimolar concentrations, the plot of $1/c$ vs. time gives a straight line for $t > 10 \text{ sec}$, *i.e.*, for times higher than that necessary for complete mixing and establishing of normal polarographic conditions.

The results of the measurements are given in Figure 2. The mean value of the rate constant in the minimum of the curve depicted in Figure 2 is $16 \pm 1.5 M^{-1} \text{ sec}^{-1}$ at 0° . The minimum value of the rate constant is reached at pH 9.25 (at 0°) and does not depend upon the ionic strength nor upon the concentration of the reactants, at least in the range of concentrations studied. The reaction is seen to be acid-base catalyzed. However, as the rate does not depend, within the limits of

(4) (a) A. A. Vlček, *J. Pure Appl. Chem.*, **10**, 61 (1965); (b) H. Matschiner, Ph.D. Thesis, Polarographic Institute, Prague, 1962.

(5) L. Simándi and F. Nagy, *Acta Chim. Acad. Sci. Hung.*, **46**, 101 (1965).

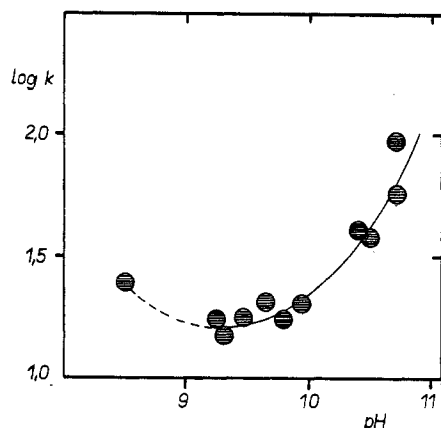


Figure 2.—pH dependence of the formal rate constant of the reaction $\text{Co}(\text{CN})_5\text{H}^{3-} + p\text{-benzoquinone}$. The points represent results of one typical run; the full curve is calculated according to eq 1.

TABLE I

KINETIC DATA ON THE REACTION BETWEEN $\text{Co}(\text{CN})_5\text{H}^{3-}$ AND $p\text{-BENZOQUINONE}$; CONCENTRATION OF REACTANTS, $10^{-3} M^a$ AT 0°

pH	C_{KCl}, M	C_{buffer}, M	$k, M^{-1} \text{sec}^{-1}$
8.53	1.0	0.1	24
9.26	1.0	0.1	17.5
9.33	0.5	0.1	15
	1.0	0.1	15
	1.5	0.1	13
9.48	1	0.1	18
9.66	1	0.05	21
	1	0.1	20
	1	0.15	20.5
9.81	1	0.1	18
9.95	1	0.1	20.3
10.40	1	0.1	40
10.52			
	1	0.1	40.5
10.70	1	0.1	58
10.80	1	0.1	92

^a The reaction was studied in the range of concentrations of reactants 8×10^{-4} to $4 \times 10^{-3} M$. Within the experimental error, no dependence upon the absolute concentration of reactants was observed.

the experimental error, upon the concentration of the buffer components (at constant pH and ionic strength), it has to be concluded that the specific H_3O^+ and OH^- catalysis takes place. The rate of the reaction does not furthermore depend upon the ionic strength nor upon the nature of cations or anions present.

The reaction can be followed only up to pH ~ 10.8 . At higher values the stability of p -quinone in solution is rather poor and the kinetics is influenced by the decomposition of p -quinone.

In solutions with pH > 9.25 the dependence of the measured rate constant k upon the pH fits the equation

$$k = 13.5 + 8.7 \times 10^4 [\text{OH}^-] \quad (1)$$

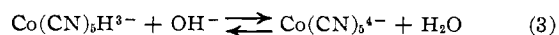
These results can be interpreted under the assumption that both $\text{Co}(\text{CN})_5\text{H}^{3-}$ and its deprotonated form, $\text{Co}(\text{CN})_5^{4-}$ take part in the reduction process. $\text{Co}(\text{CN})_5^{4-}$ has been detected as the primary product of the reduction of $\text{Co}(\text{CN})_5^{3-}$ at the dropping mercury electrode,^{4,6} and it has been shown that it behaves as a

very strong base, extracting protons from water even in rather alkaline solutions.⁴

According to this, the over-all rate of the reaction is given by

$$R = k_1[\text{quinone}][\text{Co}(\text{CN})_5\text{H}^{3-}] + k_2[\text{quinone}][\text{Co}(\text{CN})_5^{4-}] \quad (2)$$

The deprotonation of $\text{Co}(\text{CN})_5\text{H}^{3-}$ can be described by the equation



$$K = \frac{[\text{Co}(\text{CN})_5^{4-}]}{[\text{Co}(\text{CN})_5\text{H}^{3-}][\text{OH}^-]} \quad (4)$$

Combining eq 2 and 4 and assuming that equilibrium 3 is shifted strongly to the left under the given experimental conditions, we obtain

$$R = (k_1 + k_2K[\text{OH}^-])[\text{quinone}][\text{Co}(\text{CN})_5\text{H}^{3-}] \quad (5)$$

Expression 5 is in full agreement with the experimental findings for $k_1 = 13.5 M^{-1} \text{sec}^{-1}$ and $k_2K = 8.7 \times 10^4 M^{-2} \text{sec}^{-1}$.

The value of K for equilibrium 3 is not known exactly. However, on the basis of the electrochemical behavior⁶ it can be concluded that a reasonable value for K is 10^{-3} – 10^{-4} (corresponding to conventional pK values of 17–19). Using $K = 10^{-4}$, k_2 of the order $10^9 M^{-1} \text{sec}^{-1}$ is obtained as the minimum value for the rate constant for the reaction between p -benzoquinone and the $\text{Co}(\text{CN})_5^{4-}$ ion.

The observed increase of the rate constant at pH values below 9.2 and the detection of the bridge species I as one of the primary products of the reaction point to the conclusion that under these conditions the reduction of p -benzoquinone proceeds at least partly via two successive one-electron steps. Our experimental data do not make it possible to explain this reaction path in detail. The rate of the quinone reduction at pH 8.5 is much higher than the spontaneous decomposition of the hydride species at this hydrogen ion concentration. Furthermore, the electrochemical studies on reduction or oxidation of the hydride species reveal no sufficiently mobile equilibrium in which the pentacyanocobaltate(II) and hydrogen ions would take part. From this it has to be concluded that the hydrogen ion assisted path of the reaction does not involve the formation of pentacyanocobaltate(II) in a step preceding the reaction with quinone and independent of it. More probably a one-electron function of the hydride species is induced at lower pH values. Experiments are now in progress to elucidate this hypothesis.

Mechanisms of the Reactions.— p -Benzoquinone has been shown to react with pentacyanocobaltate(II) via the redox addition mechanism.¹ The same is evidently true for the reaction with pentacyanocobaltate(I). The rate constant of the reaction of $\text{Co}(\text{CN})_5^{4-}$ is at least by 10^3 higher than the corresponding rate constant of the divalent species, $\text{Co}(\text{CN})_5^{3-}$. This

(6) J. Hanzlík and A. A. Vlček, unpublished results based on the study of $\text{Co}(\text{CN})_5^{3-}$ reduction using the commutator method in strongly alkaline solutions, the study of electroreparative reduction of $\text{Co}(\text{CN})_5^{3-}$, and the spectrophotometric study of $\text{Co}(\text{CN})_5\text{H}^{3-}$ solutions.

fact can be connected with two main differences in the properties of $\text{Co}(\text{CN})_5^{4-}$ and $\text{Co}(\text{CN})_5^{3-}$. The redox potential of $\text{Co}(\text{CN})_5^{4-}-\text{Co}(\text{CN})_5^{3-}$; *i.e.*, the Co(I)-Co(II) couple, is near -1.2 V against sce.⁶ On the other hand, the redox potential of the $\text{Co}(\text{CN})_5^{3-}-\text{Co}(\text{CN})_5\text{I}^{3-}$ couple, a representative Co(II)-Co(III) couple, is *ca.* 600 mV more positive⁴ than that of the $+1-+2$ couple. This makes the over-all free energy of the process more favorable for the Co(I) complex and thus decreases the necessary activation energy.

The redox addition mechanism requires an easily accessible and sterically localized vacant electron or electron pair. In the $\text{Co}(\text{CN})_5^{3-}$ species, having square-pyramidal configuration with one unshared electron localized in the sixth position of the octahedron,^{1,7} there is still some possible shielding of this electron by weakly bonded solvent molecules. Supposing $\text{Co}(\text{CN})_5^{4-}$ has the same square-pyramidal configuration, no coordination on the sixth octahedral position is possible so that the unshared electron pair is easily accessible by the reactant.

The fact that the species $(\text{CN})_5\text{CoOC}_6\text{H}_4\text{OH}^{3-}$ is the only primary product of the reaction even at pH values ~ 9.2 , where the direct reaction of *p*-benzoquinone with the hydride species predominates, excludes the direct hydride transfer between *p*-benzoquinone and $\text{Co}(\text{CN})_5\text{H}^{3-}$ *via* a bridge mechanism. On the other hand, a mechanism with a seven-coordinate activated complex can easily explain the observed

(7) J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3356 (1967).

behavior.⁸ It can be assumed that the quinone molecule can be primarily attached with its π -antibonding orbitals to the electron pair of the cobalt-hydrogen bond, forming thus a sort of a three-center electron-deficient bond ("addition to the bond"). This process could loosen the Co-H bond and decreases also the ionization potential of the corresponding bonding electron pair making it thus available for the redox reaction. The sterical requirements for this process are rather high in agreement with the low rate of the reaction.

The most active component in the $\text{Co}(\text{CN})_5\text{H}^{3-}$ solutions is obviously the deprotonated form, the univalent cobalt species $\text{Co}(\text{CN})_5^{4-}$. This species reacts very rapidly with substrates requiring the redox addition mechanism as well as with those able to react only *via* a weak-interaction activated complex (outer-sphere mechanism).⁶ On the other hand, the hydride species $\text{Co}(\text{CN})_5\text{H}^{3-}$ is rather inactive and requires a strong-interaction activated complex. The electron pair in the Co-H bond, as in most metal-hydride bonds,⁹ is rather inactive in redox reactions. The hydrogenation reactions, carried out with the solutions of $\text{Co}(\text{CN})_5\text{H}^{3-}$, seem thus to proceed primarily as redox additions with subsequent protonations of primary products.

(8) The uniformity of the primary product makes the assumption of an insertion reaction with the six-coordinate activated complex with four cyanide ions unlikely.

(9) D. Grešová and A. A. Vlček, to be published.

Notes

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Kinetics of the Linkage Isomerization in Iron(II) Hexacyanochromate(III)

BY J. E. HOUSE, JR., AND JOHN C. BAILAR, JR.

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In 1965, Shriver, *et al.*, reported spectral evidence indicating that the $\text{Cr}^{3+}-\text{C}\equiv\text{N}-\text{Fe}^{2+}$ linkages in $\text{KFeCr}(\text{CN})_6$ readily isomerize to $\text{Cr}^{3+}-\text{N}\equiv\text{C}-\text{Fe}^{2+}$.¹ Recently, a more definitive study of the iron(II) hexacyanochromate(III) system was published, and it was shown that the system has the approximate composition $\text{Fe}_3[\text{Cr}(\text{CN})_6]_2$ or $\text{Fe}_{1.6}[\text{Cr}(\text{CN})_6](\text{OH})_{0.2}$.² It was also

shown that in air the isomerization leads to an oxidation product requiring both water and oxygen for its formation. An estimation of the rate of the linkage isomerization was made by following the change in magnetic susceptibility of the iron(II) hexacyanochromate(III) when it was heated in a helium atmosphere. We have studied the isomerization in air, and this communication reports the results of our kinetic studies.

Experimental Section

Preparation of Compounds.—The complex containing iron(II) hexacyanochromate(III) was prepared by slowly adding a solution of 2.00 g (10 mmol) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 50 ml of water to a solution of 3.25 g (10 mmol) of $\text{K}_3\text{Cr}(\text{CN})_6$ in 30 ml of water. The reddish brown precipitate was washed with water, alcohol, and acetone and air dried. *Anal.* Calcd for $\text{KFeCr}(\text{CN})_6$: Fe, 18.34; Cr, 17.16; H, 0.0. Found: Fe, 19.40; Cr, 16.86; H, 3.18. The hydrogen content, due to residual water, is similar to that reported by Shriver, *et al.*, for their preparations.³ The complex used in this work shows an Fe:Cr ratio of 1:1 while that of Shriver, *et al.*, was about 1.6:1.

(1) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, **4**, 725 (1965).

(2) D. B. Brown, D. F. Shriver, and L. H. Schwartz, *ibid.*, **7**, 77 (1968)

(3) J. H. Bigelow, *Inorg. Syn.*, **2**, 203 (1946).