insight concerning the conformational properties of the C–F bonds of organometallic substances.

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Kinetic Studies of the Reduction and Hydrogenation of Pentacyanocobaltate Complexes by Hexacyanochromate(II)[1a]

James H. Espenson*[1b] and Dale A. Holm

Contribution from the Ames Laboratory, U. S. Atomic Energy Commission, and the Department of Chemistry, Iowa State University, Ames, Iowa 50010.

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Abstract: The reaction of $Cr(CN)_6{}^{4-}$ with $Co(CN)_5Br^{3-}$ in cyanide solution occurs in two stages. The first step forms $Cr(CN)_6{}^{3-}$, $Co(CN)_5{}^{3-}$, and Br^- in a second-order reaction with a rate constant of $1.14 \pm 0.08 \times 10^5$ M^{-1} sec^{-1} (25.0°, $\mu = 1.00$ M). The second reaction occurs between $Co(CN)_5{}^{3-}$, a product of the first step, and $Cr(CN)_6{}^{4-}$ and is an important process in the first reaction only if the latter reagent is in excess over $Co(CN)_5Br^{3-}$. The reaction of $Co(CN)_5{}^{3-}$ and $Cr(CN)_6{}^{4-}$ produces $Co(CN)_5H^{3-}$, $Cr(CN)_6{}^{3-}$, and OH^- and occurs with a second-order rate constant of $2.4 \pm 0.1 \times 10^4$ M^{-1} sec^{-1} (25.0°, $\mu = 1.00$ M). Both reactions are independent of $[CN^-]$ (>0.2 M) and of $[OH^-]$. The combination of the two reactions provides a means for carrying out the catalytic hydrogenation of α,β-unsaturated compounds without molecular hydrogen, $Cr(CN)_6{}^{4-}$ serving as a reducing agent to liberate hydrogen from water *via* the intermediate hydrogenating agent $Co(CN)_5H^{3-}$.

The strongly reducing and highly reactive complex $Cr(CN)_6{}^{4-}$ is formed in solutions of Cr(II) containing excess cyanide ion.[2–5] In this work we wish to report on some kinetic studies carried out on the reactions of $Cr(CN)_6{}^{4-}$ with $Co(CN)_5X^{3-}$ complexes, work initially prompted by a desire to explore the rate patterns of outer-sphere reactions between anionic complexes. It became evident that a further unexpected reaction was occurring between the two strongly reducing species $Cr(CN)_6{}^{4-}$ and $Co(CN)_5{}^{3-}$. This latter reaction limited the number of different $Co(CN)_5X^{3-}$ complexes whose reactions could usefully be studied, but it revealed a novel aspect of the chemistry of Cr $(CN)_6{}^{4-}$, which resulted in the conversion of $Co(CN)_5{}^{3-}$ to $Co(CN)_5H^{3-}$ which is an active hydrogenation agent.

Experimental Section

Materials. Potassium hexacyanochromate(III) was prepared by the air oxidation of Cr(II) in solutions containing excess cyanide ion, precipitating $K_3Cr(CN)_6$ by addition of ethanol.[6] The spectrum of the complex was in good agreement with that reported previously.[7] Salts of hexacyanochromate(II) were not isolated because of known difficulties with its high reactivity. Solutions of $K_3Cr(CN)_6$ in excess cyanide were prepared just prior to each kinetic run and reduced with amalgamated zinc. In those rate runs where the reactant concentrations were comparable, the $Cr(CN)_6{}^{4-}$ concentrations were analyzed by injecting an aliquot into an oxygen-free solution of ferricyanide, measuring the absorbance decrease at λ 420 nm ($\Delta\epsilon = 967$ M^{-1} cm^{-1}). The spectrum of $Cr(CN)_6{}^{4-}$ shows absorption maxima at λ 327 nm (ε 8900) and 264 (6300) which agree favorably with the values established earlier, 327 (8700,[5a] 9000[5b]), 264 (5800[5a,5b]), and 227 (9700,[5a] 101,000[5b]).

The complex $K_3[Co(CN)_5Br]$ was prepared by a procedure based upon the method of Adamson.[8] Solutions of $Co(CN)_5{}^{3-}$ were prepared immediately prior to each run by injection of a $Co(ClO_4)_2$ solution into an oxygen-free solution of sodium cyanide. The method of preparation of $Cs_2Na[Co(CN)_5H]$ was that used by Banks and Pratt.[9] $NaClO_4$ was recrystallized three times before use, whereas other inorganic chemicals not specifically referred to were used as the reagent grade materials. Conductivity water was used throughout.

The unsaturated organic substrates were purified by vacuum distillation just prior to use. Solutions of each in methanol were prepared on the basis of the densities of each reagent.

Kinetic Studies. An Atom-Mech stopped-flow apparatus[10–12] was used for the study of the reactions of $Cr(CN)_6{}^{4-}$ with the $Co(CN)_5$ complexes. Studies involving $Co(CN)_5{}^{3-}$ were carried out at λ 970 nm where only this complex has an appreciable absorbance (ε ~300). Typically three or four repeat kinetic determinations were made on each set of reactant solutions.

A Cary-14 spectrophotometer was used for the study of the reactions[13] involving α,β-unsaturated organic substrates with $Co(CN)_5H^{3-}$ which was used to confirm the production of the hydrido complex.

Results

Reaction between $Cr(CN)_4{}^{4-}$ and $Co(CN)_5Br^{3-}$. The stoichiometry of the main reaction is represented by the equation

$$Cr(CN)_6{}^{4-} + Co(CN)_5Br^{3-} = Co(CN)_5{}^{3-} + Cr(CN)_6{}^{3-} + Br^- \quad (1)$$

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(1) (a) Based on the M.S. Thesis of D. A. H., Iowa State University, Nov 1969; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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(3) D. N. Hume and H. W. Stone, *ibid.*, **63**, 1200 (1941).

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(5) (a) G. Davies, N. Sutin, and K. O. Watkins, *ibid.*, **92**, 1892 (1970); (b) L. Jeftić and S. W. Feldberg, *J. Phys. Chem.*, **75**, 2381 (1971).

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(7) R. Krishnamurthy and W. B. Schaap, *ibid.*, **2**, 605 (1963).

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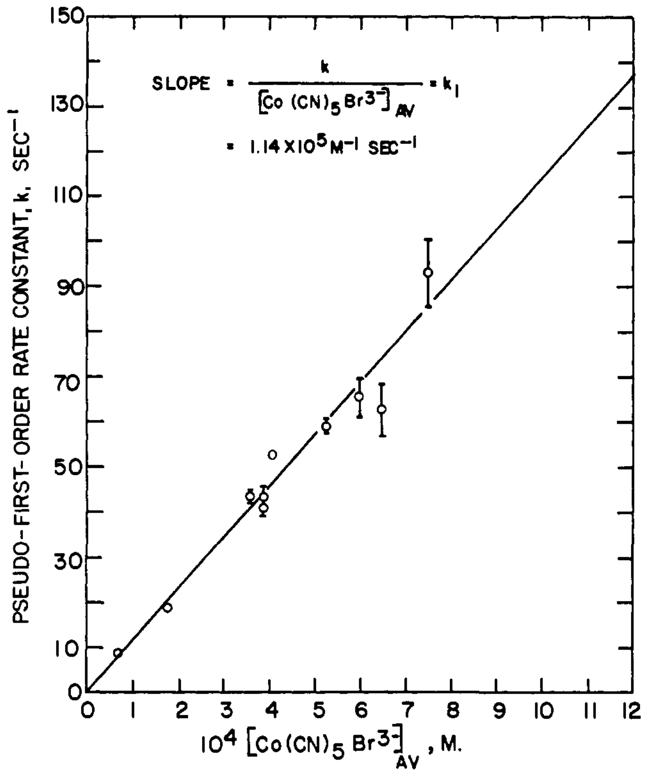

Figure 1. A plot of the pseudo-first-order rate constant for reaction 1 *vs.* $[Co(CN)_5Br^{3-}]_{av}$ including the data at all CN^- and OH^- concentrations. The error bars represent the mean deviations of repeat determinations.

A spectrophotometric titration of $Co(CN)_5Br^{3-}$ in 0.2 *M* CN^- and 0.2 *M* OH^- was carried out at λ 970 nm which is a characteristic peak for the five-coordinate species $Co(CN)_5{}^{3-}$. The absorbance increased steadily when successive portions of $Cr(CN)_6{}^{4-}$ were added until a ratio of the reactants of *ca.* 1.00 ± 0.05 was reached. After this point the absorbance steadily decreased owing to the consumption of $Co(CN)_5{}^{3-}$ by reaction with $Cr(CN)_6{}^{4-}$ as discussed in the next section. The maximum yield of $Co(CN)_5{}^{3-}$ as determined at λ 970 nm was below the theoretical value despite the 1:1 ratio in which the reagents reacted, suggesting that other cobalt complexes might simultaneously be formed or that secondary reactions leading to loss of $Co(CN)_5{}^{3-}$ might be occurring.

A second approach to the question of the reaction stoichiometry was the following. One reaction solution was made up with excess $Co(CN)_5Br^{3-}$ and subsequently exposed to air. Its spectrum agreed very closely with that of a solution containing a supposedly identical mixture of the authentic complexes $Cr(CN)_6{}^{3-}$, $Co(CN)_5{}^{3-}$, and $Co(CN)_5Br^{3-}$ which had been exposed to air.

In solutions containing excess free cyanide ions the rate of reaction 1 is given by the expression

$$-d[Cr(CN)_6{}^{4-}]/dt = k_1[Cr(CN)_6{}^{4-}][Co(CN)_5Br^{3-}] \quad (2)$$

Kinetic experiments were carried out at λ 328 nm with 0.2 *M* CN^- and 0.02 *M* OH^- with excess $Co(CN)_5Br^{3-}$ and covered the following concentration ranges: 0.88–7.6 × 10^{-4} *M* $Co(CN)_5Br^{3-}$ and 2.2–6.5 × 10^{-5} *M* $Cr(CN)_6{}^{4-}$. Many of the experiments were carried out under pseudo-first-order conditions, but several runs required the use of the integrated second-order rate expression. The value of k_1 was not dependent upon reactant concentrations over the concentration ranges chosen, which were somewhat narrow owing to the extreme air sensitivity of $Cr(CN)_6{}^{4-}$, the high reaction rate, and the necessity of avoiding interference by the second reaction to evaluate k_1 precisely. The average value of k_1 at 25.0° and μ = 1.00 *M* is 1.14 ± 0.08 × 10^5 M^{-1} sec^{-1}. Studies at λ 970 nm were rather imprecise owing to a much smaller absorbance change; one successful run gave k_1 = 1.0 ± 0.1 × 10^5 M^{-1} sec^{-1}, which indicates that the rate of appearance of $Co(CN)_5{}^{3-}$ (λ 970) is substantially the same as the rate of loss of $Cr(CN)_6{}^{4-}$ (λ 328).

The reaction rate is independent of $[CN^-]$, varied between 0.20 and 0.98 *M*, and of $[OH^-]$ between 0.02 and 0.20 *M*. All the kinetic data are summarized in Figure 1.

In a few experiments at 0.05 *M* CN^- the rate showed an erratic variation with $[OH^-]$. Under these conditions the species $Cr(CN)_6{}^{4-}$ no longer predominates, with $Cr(CN)_5H_2O^{3-}$ also of importance. Davies, *et al.*,[5] report that the reaction

$$Cr(CN)_5H_2O^{3-} + CN^- = Cr(CN)_6{}^{4-} + H_2O \quad (3)$$

has an equilibrium quotient of 9.5 M^{-1} at 25°, μ = 1 *M*. Consequently, in the kinetics experiments considered reliable, those with $[CN^-] \geq 0.20$ *M*, the Cr(II) was present largely ($\geq$66%) as the hexacyano complex.

Reaction between $Cr(CN)_6{}^{4-}$ and $Co(CN)_5{}^{3-}$. When a kinetic study of reaction 1 was done with $Cr(CN)_6{}^{4-}$ in excess, it was discovered that the following secondary reaction occurs.

$$Cr(CN)_6{}^{4-} + Co(CN)_5{}^{3-} + H_2O = Cr(CN)_6{}^{3-} + Co(CN)_5H^{3-} + OH^- \quad (4)$$

A titration of authentic $Co(CN)_5{}^{3-}$ (*i.e.*, from Co^{2+} + CN^-, rather than generation by reaction 1) with $Cr(CN)_6{}^{4-}$ in 0.05 *M* CN^- resulted in a decrease of the $Co(CN)_5{}^{3-}$ peak at λ 970 nm with the end point occurring at a ratio $[Cr(CN)_6{}^{4-}]/[Co(CN)_5{}^{3-}]$ of 1.13. Considering that both reactants are highly sensitive to traces of oxygen, this indicates a 1:1 stoichiometry for reaction 4. A similar titration of $Cr(CN)_6{}^{4-}$ with $Co(CN)_5{}^{3-}$ was made using the peak of the former at 328 nm. The first four portions of $Co(CN)_5{}^{3-}$ caused absorbance decreases averaging 0.25 absorbance units, compared with the expected change of 0.20. Because of the probable accompanying air oxidation, the loss of $Cr(CN)_6{}^{4-}$ appears to be ~20% larger than predicted by eq 4, but proof that $Cr(CN)_6{}^{4-}$ is not merely acting as a catalyst for the known[14] reduction of water by $Co(CN)_5{}^{3-}$ is evident.

$$2Co(CN)_5{}^{3-} + H_2O = Co(CN)_5OH^{3-} + Co(CN)_5H^{3-} \quad (5)$$

The cobalt compound from reaction 4 was isolated to confirm the production of the hydrido complex. The salt $Cs_2Na[Co(CN)_5H]$ was precipitated from a solution prepared by reacting a moderately concentrated solution of $Co(CN)_5Br^{3-}$ with $Cr(CN)_6{}^{4-}$ at a 1:2 ratio,[15] by addition of ethanol and cesium chloride.

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(14) (a) M. C. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc.*, 800 (1967); (b) J. P. Birk and J. Halpern, *J. Amer. Chem. Soc.*, 90, 305 (1968).

(15) This reaction, rather than reaction 4 directly, was used to prepare the reaction solution to avoid high concentrations of $Co(CN)_5{}^{3-}$ which would have generated the hydrido complex *via* reaction 5.

The ir spectrum of the solid agreed with that of a sample of authentic $Cs_2Na[Co(CN)_5H]$, as did the visible and uv spectrum recorded under oxygen-free conditions.[9,16]

In themselves, these results indicate the reaction between $Cr(CN)_6^{4-}$ and $Co(CN)_5^{3-}$ occurs in a 1:1 ratio and that some $Co(CN)_5H^{3-}$ is produced but not necessarily quantitatively. Further evidence concerning the production of $Co(CN)_5H^{3-}$ comes from experiments dealing with the hydrogenation of olefins discussed in a later section.

Kinetic studies of reaction 4 were carried out at $[CN^-] = 0.20\ M$, $[OH^-] = 0.02\ M$. Initial concentrations were $7 \times 10^{-6} \leq [Cr(CN)_6^{4-}]_0 \leq 7 \times 10^{-4}\ M$ and $1 \times 10^{-4} \leq [Co(CN)_5^{3-}] \leq 8 \times 10^{-4}\ M$. The rate measurements were made at λ 328 nm with excess $Co(CN)_5^{3-}$ except one run at λ 950 nm where $Co(CN)_5^{3-}$ was the limiting reagent. In these experiments $Co(CN)_5^{3-}$ was prepared directly in one solution reservoir, although it was later found more convenient to have Co^{2+} alone in that reservoir, $Co(CN)_5^{3-}$ being formed "instantaneously" upon mixing with the $Cr(CN)_6^{4-}$ solution containing CN^- and OH^-. This method minimized any interference from reaction 5 occurring in the stock solution.

With >10-fold excess concentrations of $Co(CN)_5^{3-}$ the reaction followed pseudo-first-order kinetics, the rate constants so computed showing a linear dependence upon $[Co(CN)_5^{3-}]$ as illustrated in Figure 2.

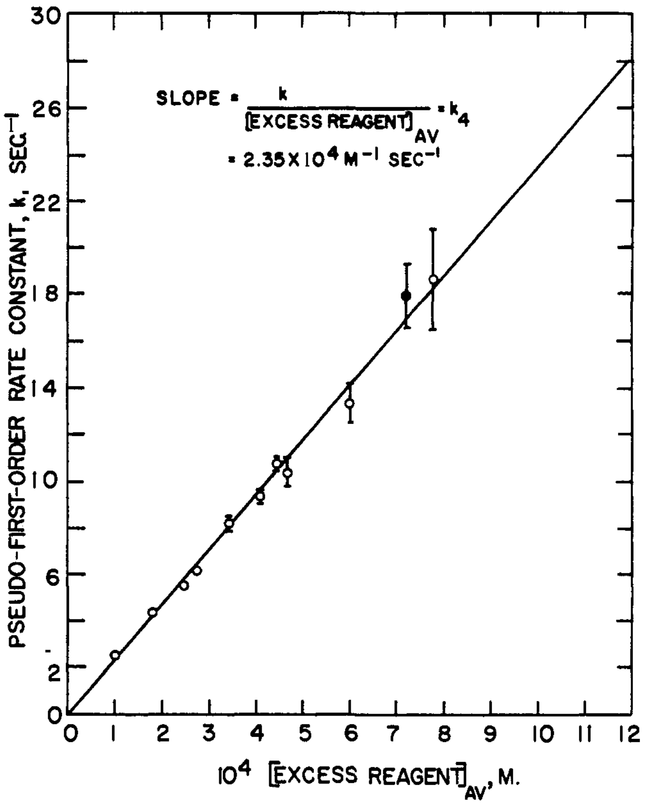

Figure 2. A plot of the pseudo-first-order rate constant for reaction 4 *vs.* the average concentration of the excess reagent including the data at all CN^- and OH^- concentrations (open circles, $Co(CN)_5^{3-}$ in excess; filled circle, $Cr(CN)_6^{4-}$ in excess).

These data are consistent with the following rate law for reaction 4

$$-d[Cr(CN)_6^{4-}]/dt = k_4[Cr(CN)_6^{4-}][Co(CN)_5^{3-}] \quad (6)$$

No rate dependence was noted on varying $[OH^-]$ between 0.01 and 0.04 *M* or upon $[CN^-]$ between 0.2 and 0.4 *M*. The average value of the rate constant was $k_4 = 2.4 \pm 0.1 \times 10^4\ M^{-1}\ sec^{-1}$ at 25.0° and $\mu = 1.00\ M$.

Hydrogenation Reactions. The complex $Co(CN)_5H^{3-}$ is known to be the active hydrogenating agent toward α,β-unsaturated compounds, the initial reaction being[13,17]

$$Co(CN)_5H^{3-} + CH_2{=}C(R)X \longrightarrow Co(CN)_5C(CH_3)(R)X^{3-} \quad (7)$$

followed by a second, slower reaction regenerating $Co(CN)_5^{3-}$. The catalytic cycle is maintained *via* the reaction

$$2Co(CN)_5^{3-} + H_2 \rightleftharpoons 2Co(CN)_5H^{3-} \quad (8)$$

which, however, is also rather slow.[14a]

Since in the present work the sequence of reactions 1 + 4

$$2Cr(CN)_6^{4-} + Co(CN)_5Br^{3-} + H_2O \longrightarrow 2Cr(CN)_6^{3-} + Co(CN)_5H^{3-} + OH^- + Br^- \quad (9)$$

generates the hydrido complex, it was of interest to learn whether the formation of the adducts as in eq 7 would occur under these conditions.

Toward this end the kinetic studies of Halpern and Wong[13] were duplicated as closely as possible to carry out comparable rate measurements on reaction 7, the rate law for which is given by

$$-d[Co(CN)_5H^{3-}]/dt = k_7[Co(CN)_5H^{3-}][CH_2{=}C(R)X] \quad (10)$$

Four of the nine compounds which Halpern and Wong investigated were studied. Because the reaction medium was not specified with regard to the concentrations of buffer components, experiments were done in the present study not only with $Co(CN)_5H^{3-}$ as generated *via* reaction 9, but with authentic $Co(CN)_5H^{3-}$ as well. Both systems were studied under identical conditions and gave comparable results as summarized in Table I.

Interpretation and Discussion

The kinetics of the reaction between $Cr(CN)_6^{4-}$ and $Co(CN)_5Br^{3-}$, eq 1, imply that the transition state is formed without loss of cyanide ions as no kinetic retardation by CN^- was noted.

The production of $Cr(CN)_6^{3-}$ rather than $Cr(CN)_5Br^{3-}$ also supports assignment of an outer-sphere mechanism to reaction 1. Halide complexes such as $Cr(CN)_5Br^{3-}$ do not appear to be known, so that it cannot be claimed that such a substance, if produced in an inner-sphere mechanism, would survive conversion to $Cr(CN)_6^{3-}$. Considering the substitution rates of Cr(III) complexes, this appears an unlikely alternative; the replacement of CN^- from $Cr(CN)_6^{3-}$ by OH^-

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[16] The ir spectrum showed absorptions at 2112, 1840, and 779 cm^{-1} in comparison with the frequencies measured on an authentic sample, 2120, 1841, and 780 cm^{-1}. The electronic spectrum showed a maximum at λ 306 nm (ε 450), and a shoulder at λ 357 (which we attribute to a $Cs_3Cr(CN)_6$ impurity); the literature spectrum has λ 305 (ε 620).[9]

[17] J. Kwiatek, *Catal. Rev.*, 1, 37 (1964).

Table I. Kinetic Studies on the Addition of $Co(CN)_5H^{3-}$ to α,β-Unsaturated Compounds[a]

Substrate	Substrate concn, M	Medium, μ	k_7, M^{-1} sec^{-1} [b] Authentic $Co(CN)_5H^{3-}$ [c]	k_7, M^{-1} sec^{-1} [b] Prepared by rxn 9
$CH_2{=}C(H)C_6H_5$	0.004–0.013	NaCN, 0.50 M	3.1 ± 1.0 (3)	3.1 ± 1.3 (3)
$CH_2{=}C(H)CN$	0.005–0.011	KCN, 0.20 M	0.61 ± 0.07 (2)	0.63 ± 0.05 (2)
$CH_2{=}C(CH_3)CN$	0.004–0.017	KCN, 0.50 M	2.26 ± 0.01 (2)	2.35 ± 0.08 (3)
$CH_2{=}C(H)\text{-}2\text{-}C_5H_4N$	0.008–0.030	KCN, 0.50 M	0.93 ± 0.06 (2)	0.75 ± 0.10 (3)

[a] Rates evaluated at 25° in 50 vol % aqueous methanol. Ionic strength adjusted to the value given by the indicated cyanide salt; added OH^-, 0.02 M. [b] Rate constant defined by eq 10, with the number of runs given in parentheses. [c] Prepared by the hydrogenation of $Co(CN)_5^{3-}$ according to the procedure of Halpern and Wong.[13]

occurs slowly.[5b] There are, however, the following reactions[18]

$$Cr(CN)_6^{4-} + Cr(CN)_5Br^{3-} \longrightarrow Cr(CN)_6^{3-} + Cr(CN)_5Br^{4-} \quad (11)$$

$$Cr(CN)_5Br^{4-} + CN^- = Cr(CN)_6^{4-} + Br^- \quad (12)$$

which would provide a reasonable route[19] for converting $Cr(CN)_5Br^{3-}$ to $Cr(CN)_6^{3-}$. The suggestion of an outer-sphere mechanism for reaction 1 rests largely on the $[CN^-]$-independent rate.

In comparison, the rate of reaction of $Co(CN)_5^{3-}$ with $Co(NH_3)_5X^{2+}$ complexes is given by[20]

$$-d[Co(III)]/dt = \{k + k'[CN^-]\}[Co(CN)_5^{3-}][Co(NH_3)_5X^{2+}] \quad (13)$$

where the first term represents the contribution of an X-bridged inner-sphere pathway, and the second corresponds to an outer-sphere reaction between $Co(NH_3)_5X^{2+}$ and $Co(CN)_6^{4-}$. The latter species is generated by an equilibrium, $Co(CN)_5^{3-} + CN^- \rightleftharpoons Co(CN)_6^{4-}$, which is rather unfavorable ($K \leq 0.1\ M^{-1}$)[20] for the low spin, d^7 Co(II) case. In contrast, Cr(II) favors six-coordination, and the predominance of an outer-sphere mechanism is not surprising. The reduction of H_2O_2 by $Cr(CN)_6^{4-}$ nonetheless proceeds by parallel outer- and inner-sphere mechanisms, the latter showing the cyanide rate retardation expected for such a mechanism owing to the equilibrium shown in reaction 3. The inner-sphere mechanism in this case produces a stable product, $Cr(CN)_5OH^{3-}$, whereas this mechanism for reaction 1 would produce $Cr(CN)_5Br^{3-}$ which is unstable with respect to $Cr(CN)_6^{3-}$ in cyanide solution.

Based on the published equilibrium quotient for reaction 3,[5a] conversion to $Cr(CN)_6^{4-}$ is not complete; at the cyanide ion concentration employed, 66–91% of the Cr(II) is present as $Cr(CN)_6^{4-}$. The cyanide independence of k_1 can be accounted for in one of two ways: either $Cr(CN)_6^{4-}$ and $Cr(CN)_5H_2O^{3-}$ have comparable rates of reduction of $Co(CN)_5Br^{3-}$, so that a $[CN^-]$ dependence is not evident, or the precision of the rate constants in these very rapid reactions did not permit the resolution of this effect. At lower $[CN^-]$, where a greater proportion of lower cyano complexes would exist, there were effects of CN^- and OH^- attributable to the formation of $Cr(CN)_5H_2O^{3-}$, although they were not studied in detail.

A comparison should be made between reaction 1 and the following process

$$Cr(CN)_6^{4-} + Cr(CN)_5OH^{3-} \longrightarrow Cr(CN)_6^{3-} + Cr(CN)_5OH^{4-} \quad (14)$$

Jeftić and Feldberg[5b] find that reaction 14 proceeds by an outer-sphere mechanism because net Cr(II)-catalyzed aquation occurs and not simply electron exchange.[21] The rate constant of reaction 14 is 184 M^{-1} sec^{-1} (25.0°, μ = 1.0 M)[5b], and its equilibrium constant[22] lies in the approximate range 0.1–10. Based on the standard potentials of Cr(II, III) and Co(II, III) in cyanide solution,[23] the estimated equilibrium constant for reaction 1 is 6×10^{10} M. The mechanism in each case appears to be outer-sphere electron transfer, for which Marcus' theory should be a valid theoretical model. On this basis the higher rate constant for reaction 1 (1.1×10^5 M^{-1} sec^{-1}) compared to reaction 14 (184 M^{-1} sec^{-1}) is reasonable considering the much higher equilibrium constant for the former reaction.

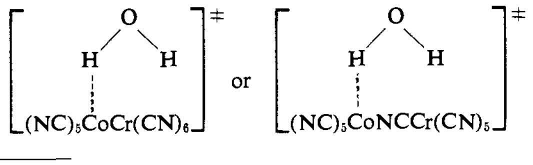
The analogy in stoichiometry between the following three reactions should be noted.

$$2Co(CN)_5^{3-} + H_2 \longrightarrow 2Co(CN)_5H^{3-} \quad (15)$$

$$2Co(CN)_5^{3-} + H_2O \longrightarrow Co(CN)_5H^{3-} + Co(CN)_5OH^{3-} \quad (16)$$

$$Co(CN)_5^{3-} + Cr(CN)_6^{4-} + H_2O \longrightarrow Co(CN)_5H^{3-} + Cr(CN)_6^{3-} + OH^- \quad (17)$$

Also, the analogy in rate expression is evident, as rate is proportional to $[Co(CN)_5^{3-}]^2[H_2]$ (eq 15), $[Co(CN)_5^{3-}]^2$ (eq 16), $[Co(CN)_5^{3-}][Cr(CN)_6^{4-}]$ (eq 17). Considering these parallels, can a similar mechanism be suggested for reaction 17? A transition state such as one of the following[24] can be envisaged.



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[18] We are grateful to a referee for suggesting this possibility.

[19] The first step is likely to occur rapidly, considering the results of Jeftić and Feldberg[5b] on an analogous reaction.

[20] J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, **85**, 2517 (1963).

[21] The radiotracer experiments have not been done to learn whether the following inner-sphere exchange process is also an important reaction in addition to 14: $^*Cr(CN)_6^{4-} + Cr(CN)_5OH^{3-} \rightarrow {}^*Cr(CN)_5OH^{3-} + Cr(CN)_6^{4-}$.

[22] K for eq 14 is based on published equilibrium data[5] and on an estimated pK_a of ~12–14 for $Cr(CN)_5H_2O^{3-}$.

[23] This computation requires not only the E^0 values for the indicated couples, but also equilibrium constants for the reactions (a) $Co(CN)_5H_2O^{2-} + Br^- \rightleftharpoons Co(CN)_5Br^{3-} + H_2O$, for which K is *ca.* 0.9 M^{-1} [R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967)] and (b) $Co(CN)_5H_2O^{2-} + CN^- \rightleftharpoons Co(CN)_6^{3-} + H_2O$, for which K is unknown. The latter value was calculated for the analogous reaction of Cr(III) complexes from available equilibrium data,[5] and for the purpose of this approximate computation the same value was assumed to apply to the Co(III) reaction.

[24] B. DeVries, *J. Catal.*, **1**, 489 (1962), suggests similar structures for the reaction of $Co(CN)_5^{3-}$ with hydrogen.

An alternative mechanism should also be considered[18]

$$\mathrm{Cr(CN)_6^{4-} + Co(CN)_5^{3-} \longrightarrow Cr(CN)_6^{3-} + Co(CN)_5^{4-}} \quad (18)$$

$$\mathrm{Co(CN)_5^{4-} + H_2O \longrightarrow Co(CN)_5H^{3-} + OH^-} \quad (19)$$

which is analogous to the mechanism proposed for the reaction of $Co(CN)_5^{3-}$ with the strongly reducing e_{aq}^-.[25] In the present case the first step would correspond to the rate-determining step, in accord with the rate law in eq 6. The second step, eq 19, would need to be more rapid than eq 18 in order that this mechanism be consistent with the kinetic data. For eq 19, the rate constant[25] is $1.0 \pm 0.1 \times 10^5\ \mathrm{sec}^{-1}$ ($t_{1/2} = 7\ \mu$sec), which is certainly much faster than eq 18. Consequently, the scheme shown in eq 18 is certainly an attractive alternative.

Considering that reaction 4 occurs in solutions in which reaction 1 is being studied, the question must be raised of whether the kinetic data for reaction 1 are affected as a consequence. Given the rate constants for reaction 1 and 4, the latter reaction would be expected to cause negligible interference with the kinetic study of the first step under the concentrations used in evaluating the kinetic behavior of the first experiment, excess $Co(CN)_5Br^{3-}$. This is consistent with our results on reaction 1.

The combined use of $Cr(CN)_6^{4-}$ and $Co(CN)_5^{3-}$ leads to hydrogenation of α,β-unsaturated molecules. Certain differences between the present case and that in which $Co(CN)_5^{3-}$ is used alone should be noted, however. Most striking of these is that the latter process involves the use of *molecular hydrogen* as a reactant, the sequence of steps being the following.

$$\mathrm{2Co(CN)_5^{3-} + H_2 \longrightarrow 2Co(CN)_5H^{3-}} \quad (20)$$

$$\mathrm{Co(CN)_5H^{3-} + CH_2{=}C(R)X \longrightarrow Co(CN)_5C(CH_3)(R)X^{3-}} \quad (21)$$

$$\mathrm{Co(CN)_5H^{3-} + Co(CN)_5C(CH_3)(R)X^{3-} \longrightarrow 2Co(CN)_5^{3-} + CH_3C(H)(R)X} \quad (22)$$

$$\text{Net}\quad \mathrm{CH_2{=}C(R)X + H_2 \longrightarrow CH_3C(H)(R)X} \quad (23)$$

In the sequence involving $Cr(CN)_6^{4-}$, however, molecular hydrogen is not used.

$$\mathrm{Cr(CN)_6^{4-} + Co(CN)_5^{3-} + H_2O \longrightarrow Cr(CN)_6^{3-} + Co(CN)_5H^{3-} + OH^-} \quad (24)$$

(followed by eq 22 and 21)

$$\text{Net}\quad \mathrm{2Cr(CN)_6^{4-} + CH_2{=}C(R)X + 2H_2O \longrightarrow 2Cr(CN)_6^{3-} + CH_3C(H)(R)X + 2OH^-} \quad (25)$$

In other words, the utilization of $Cr(CN)_6^{4-}$ results in its consumption during hydrogenation with the hydrogen being derived from the solvent, whereas with $Co(CN)_5^{3-}$ alone, molecular hydrogen is required and is consumed during the reaction.

In the scheme utilizing $Co(CN)_5^{3-}$ alone as a catalyst, the rate of hydrogenation is limited by the rate of reaction 20 which is a rather slow process.[24] The utilization of both metal complexes does not suffer from the same problem, as the initial step occurs very rapidly

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Some Extensively Rearranged Derivatives of Sulfur Tetrafluoride, Trifluoromethylsulfur Trifluoride, and Bis(trifluoromethyl)sulfur Difluoride from Hexafluoroisopropylideniminolithium Reactions

Richard F. Swindell[1a] **and Jean'ne M. Shreeve***[1b]

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843. *Received February 11, 1972*

Abstract: Isolation of six extensively rearranged products (I–VI) from reactions of sulfur tetrafluoride with hexafluoroisopropylideniminolithium demonstrates that simple, metathetical reactions do not occur. A possible mechanism is proposed. Similar rearranged products (VII–IX) form from the lithium salt with CF_3SF_3 and $(CF_3)_2SF_2$. Long-range coupling of nuclei separated by ten σ bonds is observed in the ^{19}F nmr spectrum of III.

Reaction of sulfur tetrafluoride and hexafluoroisopropylideniminolithium does not follow the previously predictable metathesis reactions observed with inorganic chlorides and fluorides.[2–4] Instead, the generation of $(CF_3)_2CFN{=}SF_2$ (I) *in situ* by the action of $LiN{=}C(CF_3)_2$ on SF_4 results in the formation of five new compounds each of which arises directly or indirectly from attack of the lithium salt on the sulfur difluoride imide. Thus

$$\mathrm{SF_4 + LiN{=}C(CF_3)_2 \longrightarrow}$$
$$\mathrm{(CF_3)_2CFN{=}SF_2}\ \text{(I)}$$
$$\mathrm{(CF_3)_2CFN{=}S{=}NCF(CF_3)_2}\ \text{(II)}$$
$$\mathrm{(CF_3)_2CFN{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2}\ \text{(III)}$$
$$\mathrm{(CF_3)_2C{=}NC(CF_3)_2N{=}S{=}NC(CF_3)_2N{=}C(CF_3)_2}\ \text{(IV)}$$
$$\mathrm{(CF_3)_2C{=}NC(CF_3)_2N{=}C(CF_3)_2}\ \text{(V)}$$
$$\mathrm{[(CF_3)_2C{=}N]_2S{=}NH}\ \text{(VI)}$$

Isolation of each of the new products and subsequent

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[1] (a) NDEA Graduate Fellow; (b) Alfred P. Sloan Foundation Fellow.

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