fact can be connected with two main differences in the properties of Co(CN)$_5^{4-}$ and Co(CN)$_5^{3-}$. The redox potential of Co(CN)$_5^{4-}$–Co(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 Co(CN)$_5^{3-}$–Co(CN)$_5$I^{3-} couple, a representative Co(II)–Co(III) couple, is *ca.* 600 mV more positive[4] 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 Co(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 Co(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 (CN)$_5$CoOC$_6$H$_4$OH^{3-} is the only primary product of the reaction even at pH values $\sim$9.2, where the direct reaction of *p*-benzoquinone with the hydride species predominates, excludes the direct hydride transfer between *p*-benzoquinone and Co(CN)$_5$H^{3-} *via* a bridge mechanism. On the other hand, a mechanism with a seven-coordinate activated complex can easily explain the observed 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 Co(CN)$_5$H^{3-} solutions is obviously the deprotonated form, the univalent cobalt species Co(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 Co(CN)$_5$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 Co(CN)$_5$H^{3-}, seem thus to proceed primarily as redox additions with subsequent protonations of primary products.

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

(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)

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In 1965, Shriver, *et al.*, reported spectral evidence indicating that the $\mathrm{Cr^{3+}{-}C{\equiv}N{-}Fe^{2+}}$ linkages in KFeCr(CN)$_6$ readily isomerize to $\mathrm{Cr^{3+}{-}N{\equiv}C{-}Fe^{2+}}$.[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 Fe$_3$[Cr(CN)$_6$]$_2$ or Fe$_{1.6}$[Cr(CN)$_6$](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 FeCl$_2\cdot$4H$_2$O in 50 ml of water to a solution of 3.25 g (10 mmol) of K$_3$Cr(CN)$_6$[3] in 30 ml of water. The reddish brown precipitate was washed with water, alcohol, and acetone and air dried. *Anal.* Calcd for KFeCr(CN)$_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.[2] 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.

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(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).

Kinetics.—Samples of the iron(II) hexacyanochromate(III) complex were placed in narrow Pyrex tubes in an aluminum holder and the assembly was placed in an oil bath at the desired temperature. The samples were heated without exclusion of air with the bath temperature constant to within ±0.2°. At desired times, samples were removed, crushed while dry, and made into mulls in Nujol. The infrared spectra were obtained using a Beckman IR 8 infrared spectrophotometer with an auxiliary recorder for scale expansion and amplification. Mulls were prepared so that no sample had a transmittance less than 70%. Under these conditions, absorbance is almost a linear function of transmittance so these areas were used directly. The slight errors introduced were thus minimized since ratios were used. The areas of the peaks with maxima at 2168 cm^{-1} (the cyanide stretch in $\mathrm{Cr^{3+}—C{\equiv}N—Fe^{2+}}$ bonds) and at 2092 cm^{-1} (the cyanide stretch in $\mathrm{Cr^{3+}—N{\equiv}C—Fe^{2+}}$ bonds) were determined by graphical integration.

Although it was not possible to prepare mulls of exactly the same thickness, the total absorption of the two peaks remained approximately constant. If the extinction coefficients were quite different for the two types of cyanide groups, the total areas would show a trend for the samples used in a given run. Thus, we have taken the extinction coefficients of the two types of cyanide groups to be equal and assumed the peak areas to be proportional to the number of bonds of each type.

Since the reaction studied is

$$\underset{\mathrm{A}}{\mathrm{Cr^{3+}—C{\equiv}N—Fe^{2+}}} \rightarrow \underset{\mathrm{B}}{\mathrm{Cr^{3+}—N{\equiv}C—Fe^{2+}}}$$

we may write

$$A_0 + B_0 = C = A_t + B_t \qquad (1)$$

where A_0 and B_0 are initial numbers of bonds of types A and B, respectively, A_t and B_t are the numbers at time t, and C is a constant. For a reaction which is second order in bonds of type A

$$\frac{\mathrm{d}B}{\mathrm{d}t} = k'A^2 = k'(C - B)^2 \qquad (2)$$

Integrating, multiplying by C, and substituting

$$\frac{A_t + B_t}{A_t} = kt + \frac{A_0 + B_0}{A_0} \qquad (3)$$

where $k = k'C$. Simplifying

$$\frac{B_t}{A_t} = kt + \frac{B_0}{A_0} \qquad (4)$$

Accordingly, plots of B_t/A_t *vs.* t should be linear with slopes k. If the extinction coefficients are not equal, the k values all differ by a factor equal to the ratio of the extinction coefficients. While this type of measurement does not permit a determination of the number of bonds of either type, the ratio can be determined easily even from mulls of different thicknesses.

Results and Discussion

The ratio B_t/A_t gives the ratio of the number of $\mathrm{Cr^{3+}—N{\equiv}C—Fe^{2+}}$ linkages to the number of $\mathrm{Cr^{3+}—C{\equiv}N—Fe^{2+}}$ linkages, the bond ratio. Figure 1 shows plots of the bond ratio *vs.* time. The slopes of the curves give the relative rates of isomerization. It is apparent that the rate plots for a given temperature are linear over a wide range of bond ratio. The slopes were calculated by a computer least-squares routine to give the rate constants at several temperatures. These are 0.715 × 10^{-4}, 1.43 × 10^{-4}, 2.56 × 10^{-4}, 3.78 × 10^{-4}, and 6.75 × 10^{-4} sec^{-1} at 50, 55, 60, 65, and 70°, respectively. The differences in intercepts in Figure 1 indicate that the starting material undergoes some isomerization, even at room temperature, since the order of increase of bond ratio when heating was begun is the same as the order in which the runs were performed. A total time of about 1 week elapsed between the preparation of the complex and the completion of all of the kinetic runs. The Arrhenius activation energy calculated by a least-squares treatment of the rate constants is 24.1 ± 1.6 kcal/mol. Previously reported values for the rate constant at 50° and the activation energy are 1.0 × 10^{-4} sec^{-1} and 17 kcal/mol, respectively, for the reaction carried out in an inert atmosphere.[2]

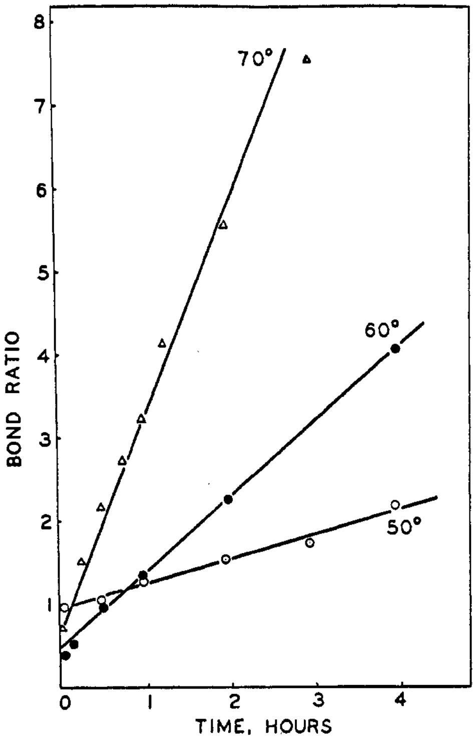

Figure 1.—Rate plots of bond ratio *vs.* time.

A reaction second order in bonds of type $\mathrm{Cr^{3+}—C{\equiv}N—Fe^{2+}}$ implies that in the rate-determining step two cyanides "flip" instead of one. This could be due to the *cis* or *trans* influence of a flipping cyanide on a second cyanide in the *cis* or *trans* position, respectively. In either case, the activated complex should have a coordination number of 4 and should be either square planar if a *trans* pair of cyanides "flips" or distorted tetrahedral if a *cis* pair "flips." During all runs the compound changed from reddish brown to dark green. This change occurred within a few minutes at 70° and within a few hours at 50°.