tion of hexane. Nitrile complexes **3d** and **3e** were recrystallized from tetrahydrofuran–ether. The melting points of these substances were not changed by repeated recrystallization, but the relative intensities of the three closely spaced infrared peaks in the 1660-cm.$^{-1}$ region changed decidedly.

Chlorocarbonylbis(triphenylphosphine)(tetrafluoroethylene)iridium(I) (**4**). A 200-ml. Carius tube containing 4.0 g. of tetrafluoroethylene and 95 ml. of a saturated solution of chlorocarbonylbis(triphenylphosphine)-iridium(I)[7] in toluene was agitated at 25° for 1 week. The brilliant yellow solution slowly became colorless. The solvent was removed at reduced pressure to leave a faintly yellow solid. Recrystallization from toluene under TFE pressure (3 atm.) gave white crystals of the TFE complex **4**. The P^{31} n.m.r. spectrum of a saturated benzene solution contained a single broad peak at +16.4 p.p.m. (*vs.* 85% H$_3$PO$_4$ external reference).

Pyrolysis of Complex **4**. In a system of known volume attached to a manometer, 0.0903 g. (0.111 mmole) of the above product was slowly heated. Gas evolution was slow at 100°; equilibrium was quickly reached at 130°. The gas (0.08 mmole) was characterized by its infrared and mass spectra as TFE. The bright yellow residual solid appeared to be pure chlorocarbonylbis-(triphenylphosphine)iridium(I) on the basis of its infrared spectrum; it weighed 0.084 g. (97%). The solid did not reabsorb TFE as it cooled.

Chlorocarbonylbis(triphenylphosphine)(hexafluoro-2-butyne)iridium (**5**). A suspension of 0.78 g. of chloro-carbonylbis(triphenylphosphine)iridium(I)[7] in 20 ml. of toluene was stirred under 700 mm. pressure of hexafluoro-2-butyne for 16 hr. The brilliant yellow starting material dissolved, and a pale yellow solid crystallized. The solid was collected and dried for 4 hr. at 25° at a pressure of 10^{-3} mm. Some toluene remained in the crystal lattice as indicated by the elemental analyses and the pyrolysis experiment below.

Reversible Pyrolysis of Complex **5**. An 0.816-g. (0.867 mmole) sample of the hexafluorobutyne complex (**5**) was pyrolyzed under high vacuum in a test tube sealed to a vacuum manifold. No gas evolution was noted below 85°. At 110° a rapid pressure increase occurred and equilibrium was reached at 110 mm. (corrected to 25°) within 2 hr. The mixture was allowed to stand at room temperature overnight. The pressure fell to 30 mm. Heating to 110° caused a pressure rise to 110 mm. The gas evolution by weight and volume change was 0.87 mmole. The gas was characterized by its infrared and mass spectra as hexafluoro-2-butyne containing a small amount of toluene. During the pyrolysis the color of the solid changed from off-white to bright yellow. The infrared spectrum of the yellow residue was identical with that of chlorocarbonylbis(triphenylphosphine)iridium(I); 0.663 g. (98%) was recovered. Exposure of the recovered solid to oxygen did not lead to gas absorption. However, re-exposure to hexafluoro-2-butyne resulted in absorption of 0.56 mmole of the gas.

Tetrafluoroethylenetris(triphenylphosphine)nickel(0) (**6**). A solution of 1.0 g. of ethylenebis(triphenylphosphine)nickel(0)[8] in 10 ml. of *m*-xylene was treated with tetrafluoroethylene at atmospheric pressure. The red solution immediately became brown, and yellow crystals separated. The crystals were filtered under nitrogen, washed three times with benzene, and dried under reduced pressure; the yield was about 0.4 g. The product decomposed when heated above 150° and was very sensitive to air. The P^{31} n.m.r. spectrum determined at 19.2 Mc/sec. on a saturated solution in benzene contained a single peak at −20.3 p.p.m. relative to 85% H$_3$PO$_4$ as an external standard.

Kinetics of the Reactions of Pentacyanocobaltate(II) with Organic Halides

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Pentacyanocobaltate(II) reacts with organic halides in aqueous solution to form pentacyanoorganocobaltate(III) compounds according to the reaction, 2Co(CN)$_5$$^{3-}$ + RX → Co(CN)$_5$R^{3-} + Co(CN)$_5$X^{3-}. The kinetics of this reaction were examined for a number of organic halides and found in each case to be first order in pentacyanocobaltate(II) and in the halide. Second-order rate constants at 25° ranged from 2.5 × 10^{-4} M^{-1} sec.$^{-1}$ for Cl–CH$_2$CO$_2$$^-$ to 9 × 10^4 M^{-1} sec.$^{-1}$ for I–CH$_2$COOCH$_3$, the general trend reflecting an inverse dependence of the rate constant on the carbon–halogen bond strength. Activation parameters were determined for a number of the reactions. The results are interpreted in terms of the stepwise mechanism, Co-

$(CN)_5{}^{3-} + RX \rightarrow Co(CN)_5X^{3-} + R \cdot$ *(rate determining)*, followed by $Co(CN)_5{}^{3-} + R \cdot \rightarrow Co(CN)_5R^{3-}$.

Introduction

We have previously reported[1] that pentacyanocobaltate(II) reacts with organic halides to form stable organocobalt compounds according to eq. 1. The

$$2Co^{II}(CN)_5{}^{3-} + RX \longrightarrow Co^{III}(CN)_5R^{3-} + Co^{III}(CN)_5X^{3-} \quad (1)$$

formation of pentacyanoorganocobaltate(III) compounds, both by this method and by an alternative route involving the addition of Co(CN)$_5$H^{3-} to acti-

(1) J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **86**, 2311 (1964).

vated olefins, has also been observed by Kwiatek and Seyler.[2] In this paper we describe kinetic studies on reaction 1 between $Co(CN)_5^{3-}$ and a number of water-soluble organic halides. Of related interest are some recent kinetic studies on the analogous reactions of aquochromium(II) with organic halides leading to the formation of pentaaquoorganochromium(III) compounds.[3-5]

Experimental Section

Materials. Sodium iodomethanesulfonate, prepared by the method of Palmer,[6] was recrystallized several times from alcohol and dried under vacuum; the final product gave a negative test for iodide with silver nitrate. *Anal.* Calcd. for CH_2ISO_3Na: I, 52.01. Found: I, 51.91. α-Bromoacetamide was prepared by treating ammonia with α-bromoacetyl bromide (both in dry ether solutions) at 0°; the product was recrystallized several times from petroleum ether (b.p. 30–60°), m.p. 87° (lit. 90°). *Anal.* Calcd. for C_2H_4NOBr: Br, 57.92. Found: Br, 57.87. Sodium 4-(bromomethyl)benzoate was prepared by neutralizing the corresponding acid (obtained from Aldrich Chemical Co.) with sodium carbonate and evaporating under vacuum. *Anal.* Calcd. for $C_8H_6O_2$-BrNa: Br, 33.7. Found: Br, 32.2. This compound hydrolyzed readily in aqueous solution and gave a slight positive bromide test with silver nitrate. *dl-α,β*-Dibromosuccinic acid was prepared by treating bromine with maleic acid in ether solution and was recrystallized from benzene and acetone, m.p. 166–168° (lit. 166–167° dec.). *Anal.* Calcd. for $C_4H_4O_4Br_2$: Br, 57.93. Found: Br, 56.72. α-Iodopyridine was prepared by treating the diazonium compound of α-aminopyridine in acetic acid with potassium iodide, steam distilling the product, and extracting the distillate with ether. *Anal.* Calcd. for C_5H_4NI: I, 61.91. Found: I, 61.64. Iodofumaric acid was prepared by treating the monopotassium salt of acetylenedicarboxylic acid with aqueous hydriodic acid at 60°. The solution was acidified with dilute sulfuric acid and the product extracted with ether and recrystallized from petroleum ether, m.p. 190° (lit. 194°). *Anal.* Calcd. for $C_4H_3O_4I$: I, 52.44. Found: I, 51.50.

Methyl α-iodoacetate, b.p. 165–167° (lit. 169–171°) (*Anal.* Calcd. for $C_3H_5O_2I$: I, 63.46. Found: I, 63.49), and methyl β-iodopropionate, b.p. 186° (lit. 188°) (*Anal.* Calcd. for $C_4H_7O_2I$: I, 59.30. Found: I, 59.25) were prepared by passing diazomethane through ether solutions of α-iodoacetic acid and β-iodopropionic acid, respectively, at 0°.

The following were purified by recrystallization from petroleum ether (b.p. 30–60°): α-iodoacetic acid, m.p. 81.5° (lit. 82°); β-iodopropionic acid, m.p. 82° (lit. 82°) (*Anal.* Calcd. for $C_3H_5O_2I$: I, 63.46. Found: I, 63.46); α-iodoacetamide, m.p. 93° (lit.

93°) (*Anal.* Calcd. for C_2H_4NOI: I, 68.60. Found: I, 68.96); bromoacetic acid, m.p. 48.5° (lit. 50°); β-bromopropionic acid, m.p. 62° (lit. 62.5°).

The following were purified by redistillation: α-bromopropionic acid, b.p. 197–199° (741 mm.) (lit. 203.5°); methyl α-bromoacetate, b.p. 142.5° (742 mm.) (lit. 144° dec.). *Anal.* Calcd. for $C_3H_5O_2Br$: Br, 52.24. Found: Br, 52.33.

The following were commercial reagent grade chemicals and were used without further purification: *meso-α,β*-dibromosuccinic acid, m.p. ~260° (lit. 260–270°, sublimes with decomposition); chloroacetic acid; methyl α-chloroacetate, b.p. 131.5° (lit. 131.5°); α,β-dibromopropionic acid, m.p. 64° (lit. 64°); α-chloroacetamide, m.p. 118° (lit. 119.5°); dichloroacetic acid; trichloroacetic acid; *meso-α,β*-dichlorosuccinic acid; bromosuccinic acid, m.p. 163–164° (lit. 164°).

Cobaltous perchlorate, sodium perchlorate, sodium cyanide, and sodium hydroxide were all reagent grade chemicals. Distilled water was used in the preparation of all solutions.

Kinetic Measurements. The procedure used for the kinetic measurements depended upon the rate of the reaction. The rates of reactions with half-lives shorter than about 10 sec. (generally corresponding to $k >$ 1 M^{-1} sec.$^{-1}$) were measured with a stopped-flow apparatus previously described.[7,8] The apparatus was equipped with two detectors, an EMI 6256 (S.13) photomultiplier and a Dumont K2776 (S.1) photomultiplier which covered the wave length ranges 200–500 and 500–1200 mμ, respectively.

In a typical stopped-flow experiment the two initial solutions, prior to mixing in the stopped-flow apparatus, contained the following reagents: (solution A) the organic halide, cobaltous perchlorate (generally between 10^{-2} and 10^{-4} M), and sufficient sodium perchlorate to make the ionic strength 0.2 M; (solution B) sodium cyanide (the concentration of which was equal to or greater than five times the concentration of cobalt(II) in solution A), sodium hydroxide at the same concentration as sodium cyanide to suppress hydrolysis of the latter, and sufficient sodium perchlorate make the ionic strength 0.2 M. Both solutions were deoxygenated with purified nitrogen and pre-equilibrated to the reaction temperature prior to mixing. Temperature control in the stopped-flow apparatus was about ±0.2°.

The $Co(CN)_5^{3-}$ was thus generated in the stopped-flow apparatus upon mixing of the two solutions, its formation from Co^{2+} and CN^- being complete in the time of mixing (approximately 1 msec.) and much faster than the reaction of $Co(CN)_5^{3-}$ with any of the organic halides studied. At the pH of the reaction solutions (generally >12) dissociation of all the halogenated organic acids was substantially complete so that the observed reactions of $Co(CN)_5^{3-}$ in these cases were with the corresponding anions.

The reactions were generally followed by measuring the increase in absorbance of the halopentacyanocobaltate(III) product, using one of the following absorption bands: $Co(CN)_5I^{3-}$, λ_{max} 495 mμ (ϵ_{max} 117)

(2) (a) J. Kwiatek and J. K. Seyler, "Proceedings of the 8th International Conference on Coordination Chemistry, Vienna," Springer-Verlag, Vienna, 1964, p. 308; (b) J. Kwiatek and J. K. Seyler, *J. Organomet. Chem.*, 3, 421 (1965); (c) M. J. Mays and G. Wilkinson, *Nature*, 203, 1167 (1964); (d) R. Mason and D. R. Russell, *Chem. Commun.* (London), 182 (1965).
(3) C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, 85, 2768 (1963).
(4) W. C. Kray, Jr., and C. E. Castro, *ibid.*, 86, 4603 (1964).
(5) J. K. Kochi and D. D. Davis, *ibid.*, 86, 5264 (1964).
(6) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, Cambridge, 1954, p. 357.

(7) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, 86, 1019 (1964).
(8) N. Sutin and G. L. Dulz, *Inorg. Chem.*, 2, 917 (1963).

or 326 mμ (ϵ_{max} 4100); $Co(CN)_5Br^{3-}$, λ_{max} 395 mμ (ϵ_{max} 195); $Co(CN)_5Cl^{3-}$, λ_{max} 388 mμ (ϵ_{max} 220). For the monohalides, good agreement was always found between the rate of formation of this product and the rate of disappearance of $Co(CN)_5^{3-}$ followed by the decrease in the absorbance of the latter in the wave length range 850 to 960 mμ [λ_{max} 967 mμ (ϵ_{max} 298) for $Co(CN)_5^{3-}$]. Only in one case involving the reaction of $Co(CN)_5^{3-}$ with p-$BrCH_2C_6H_4CO_2^-$ did the spectral characteristics of the organocobalt species (corresponding to an intense absorption band at 312 mμ, similar to that found[1] previously for pentacyanobenzylcobaltate(III)) permit the reaction to be followed by the appearance of this product.

The rates of the slower reactions, i.e., those having a half-life greater than about 10 sec. (generally $k < 1 M^{-1}$ sec.$^{-1}$), were measured conventionally using a Cary 14 recording spectrophotometer with a cell compartment thermostated at 25 $\pm$ 0.5°. The reaction was initiated by rapidly injecting an oxygen-free solution containing sodium cyanide and sodium hydroxide from a hypodermic syringe through a serum cap into a nitrogen-filled spectrophotometer cell containing a solution of the organic halide, cobaltous perchlorate (typically 4 $\times$ 10^{-3} M), and sufficient sodium perchlorate to give a final ionic strength of 0.2 M. Using this procedure it was possible to measure the rates of reactions with half-lives down to about 4 sec. Most of these reactions were followed by the decrease in absorbance of $Co(CN)_5^{3-}$, rather than the formation of $Co(CN)_5X^{3-}$ (X = I, Br, or Cl) because of possible interference, in the case of slow reactions, from hydrolysis of the latter product. The reaction of $Co(CN)_5^{3-}$ with $ICH_2CH_2CO_2^-$ was studied both in the stopped-flow apparatus and in the Cary spectrophotometer, the two methods yielding rate constants which agreed to within 5%.

It was not feasible to extend these rate measurements to very slow reactions, with half-lives exceeding 30 min., because of the instability of $Co(CN)_5^{3-}$ in aqueous solution, arising from the slow reaction, $2Co(CN)_5^{3-} + H_2O \rightarrow Co(CN)_5OH^{3-} + Co(CN)_5H^{3-}$.

Spectral Measurements. Ultraviolet and visible spectra were recorded with a Cary Model 14 spectrophotometer. N.m.r. spectra were determined with a Varian A-60 spectrometer. Infrared spectra were recorded with a Beckman IR-7 spectrophotometer.

Microanalyses were performed by Mr. W. Saschek of the Department of Chemistry, University of Chicago.

Results and Discussion

Products and Stoichiometry of the Reaction. In general, the pentacyanoorganocobaltate(III) products of the reactions studied were not isolated in pure form although a number of such products have been previously[1] isolated and characterized. In each case, however, the products were qualitatively characterized by precipitating the combined potassium salts of both the pentacyanohalocobaltate(III) and pentacyanoorganocobaltate(III) ions which are formed in the reaction and determining the infrared spectrum of the combined product in a KBr pellet. In each case the spectrum exhibited two distinct CN stretching bands of approximately equal intensity, one in the range of 2117 to 2134 cm.$^{-1}$ corresponding to $Co(CN)_5X^{3-}$ (X = Cl,

Br, or I) and one in the range 2094 to 2113 cm.$^{-1}$ characteristic of pentacyanoorganocobaltate(III) species (Table I). This method was also used by Kwiatek and Seyler[2b] to characterize the products of the reactions of $Co(CN)_5^{3-}$ with a number of other organic halides.

More quantitative evidence for the stoichiometry of the reactions was provided by the following observations. (i) A 0.25 M solution of $Co(CN)_5^{3-}$ at 0° was treated with an equal volume of 0.125 M ICH_2COO^- under nitrogen. Comparison of the intensity of the $-CH_2-$ proton resonance, appearing at τ 8.25 p.p.m. and identified with $Co(CN)_5CH_2COO^{4-}$, with the intensity of the CH_3 proton resonance due to a known concentration of added sodium acetate, demonstrated that the yield of $Co(CN)_5CH_2COO^{4-}$ exceeded 95%. (ii) In the reactions of $Co(CN)_5^{3-}$ with organic iodides, the yield of $Co(CN)_5I^{3-}$ could readily be determined spectrophotometrically and corresponded in every case to 50% of the initial $Co(CN)_5^{3-}$ when the organic iodide was present in excess. The analogous demonstration was generally not possible for the corresponding bromides and chlorides because the spectra of $Co(CN)_5Cl^{3-}$ and $Co(CN)_5Br^{3-}$ could not be separated from the pentacyanoorganocobaltate(III) products.

Only in one case (in addition to those cited earlier[1]) was the organocobalt product recovered in pure form. The reaction of $Co(CN)_5^{3-}$ with α-iodopyridine yielded, by repeated fractional recrystallization from ethanol–ether–water mixtures a sample of $Na_3[Co(CN)_5C_5H_4N]$ (*Anal.* Calcd.: C, 35.7; H, 1.20; N, 25.0; Co, 17.5. Found: C, 35.4; H, 1.6; N, 25.2; Co, 17.3). An aqueous solution of the compound exhibited two intense absorption bands having maxima at 285 and 248 mμ (ϵ_{max} 5.5 $\times$ 10^3 and 5 $\times$ 10^3, respectively). Thermal decomposition yielded α,α-pyridine together with other unidentified organic products. Reaction with iodine yielded α-iodopyridine (identified by n.m.r.) but, in contrast to the pentacyanoorganocobaltate(III) compounds reported earlier, the α-pyridyl compound appeared to be stable in acid solutions. The proton magnetic resonance spectrum obtained in D_2O solution was of the AKRX type, consistent with the structure
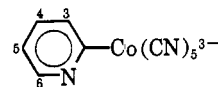
and analyzable on an entirely first-order basis to give the following coupling constants (all $\pm$0.2 c.p.s.) and chemical shifts (all $\pm$0.05 p.p.m.): $J_{34} = 8.0$, $J_{35} = 1.6$, $J_{36} = 0.8$, $J_{45} = 7.3$, $J_{46} = 2.2$, $J_{56} = 5.2$ c.p.s.; τ_3 2.20, τ_4 2.82, τ_5 3.16, τ_6 1.84 p.p.m.

In contrast to the reactions with the monohalides, the reactions of $Co(CN)_5^{3-}$ with *meso* or dl-α,β-dibromosuccinate did not yield any organocobalt compound but rather $Co(CN)_5Br^{3-}$ and fumarate[9] (identified by infrared and n.m.r.) according to the stoichiometry

$$2Co(CN)_5^{3-} + ^-OOCCHBrCHBrCOO^- \longrightarrow$$
$$2Co(CN)_5Br^{3-} + ^-OOCCH{=}CHCOO^- \quad (2)$$
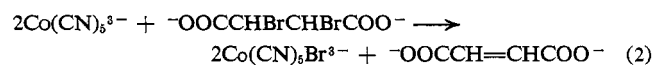
Similarly, the reaction of $Co(CN)_5^{3-}$ with α,β-dibromopropionate yielded $Co(CN)_5Br^{3-}$ and acrylate. The course of these reactions will be considered separately.

(9) It was established that maleate is not isomerized to fumarate under the prevailing conditions.

Infrared Spectra of Pentacyanocobaltate(III) Complexes. Pentacyanocobaltate(III) complexes generally exhibit a single fairly broad band in the CN stretching region which may be an unresolved composite of the three CN stretching bands expected on the basis of C_{4v} symmetry. The positions of these bands for the products of the present reactions, along with those of some related complexes for comparison, are listed in Table I.

Table I. CN Stretching Frequencies of Various Pentacyanocobaltate(III) Complexes, $Co^{III} (CN)_5-X$

-X	CN stretching frequency, (±3) cm.$^{-1a}$
-CH₃	2094^b
-CH₂CH₃	2094^b
-CH₂C₆H₅	2093^b
-CH₂CONH₂	2103
-CH₂COO⁻	2106
-CH₂COOCH₃	2105
-CH₂CH₂COO⁻	2097
-CH₂SO₃⁻	2113 (2097 sh)
-CH₂-◯-COO⁻	2106
-CH₂CH₂COOCH₃	2096
-CHCOO⁻ | CH₃	2103
-CHCOO⁻ | CH₂COO⁻	2106
-◯-N	2110
-Cl	2124
-Br	2125
-I	2117
-CN	2134
-OH₂	2128
-H	2098

^{a} Measured on the potassium salt in KBr pellet, except for Co-(CN)₅H³⁻ which was measured in aqueous solution using cells with calcium fluoride windows. An aqueous solution of Co(CN)₅³⁻ exhibited a CN stretching frequency at 2083 cm.⁻¹. ^{b} From ref. 1.

The CN stretching frequencies of the organocobalt complexes are seen to be significantly lower (ranging from 2094 to 2113 cm.⁻¹) than those of typical inorganic complexes which generally fall in the range 2125 ± 10 cm.⁻¹. Lowering of the CN stretching frequencies in these complexes is believed to result from increasing back-donation of electrons from the cobalt to the cyanide ligands, reflecting in turn the enhanced electron donor power of the organic (and hydride) ligands relative to the halides or water. Among the organic ligands the trend of the frequencies also is to increase with increasing electron-withdrawing power of the substituents attached to the carbon ligands, e.g., $\nu_{Co-CH_3} < \nu_{Co-CH_2CONH_2} < \nu_{Co-CH_2COO^-}$, etc. Analogous trends have been observed for the CO stretching frequencies of Mn(CO)₅X compounds (which are isoelectronic with the corresponding $Co^{III}(CN)_5X$ complexes) and have been similarly interpreted.[10,11]

Kinetics and Mechanism. The disappearance of Co(CN)₅³⁻ and appearance of the products were found

(10) W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961).
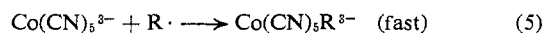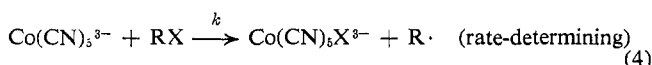(11) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

in each case to follow a second-order rate law, first order each in Co(CN)₅³⁻ and in the organic halide. Anticipating the proposed interpretation, we define the second-order rate constant k in terms of the rate law

$$-d[Co(CN)_5{}^{3-}]/dt = 2k[Co(CN)_5]^{3-}][RX] \quad (3)$$

In the kinetic experiments the initial Co(CN)₅³⁻ concentration was generally in the range 10⁻² and 10⁻⁴ and the concentration of organic halide in sufficiently large (at least tenfold) excess so that the individual kinetic plots were of pseudo first order. The initial Co(CN)₅³⁻ concentration was varied over at least a twofold range and the initial RX concentration over a tenfold range, to establish the independence of k of both concentrations. It was also established that the rate is independent of the OH⁻ concentration, above pH 10, of the excess CN⁻ concentration and (for the reactions of organic iodides) of added sodium iodide.

Values of k obtained in this way are listed in Table II. Second-order kinetic behavior as described above was confirmed for all of these reactions except those for which the results are denoted as preliminary and which are based on incomplete studies in which the initial concentrations were not varied sufficiently to establish second-order behavior. Values of the activation parameters, where determined, are listed in Table III.

The second-order kinetics, along with the observed dependence of the rate constant on variation of the organic halide, support the stepwise mechanism for these reactions proposed by Kwiatek and Seyler[2b] in which the rate-determining step is the abstraction of a halogen atom by Co(CN)₅³⁻ to generate an organic free radical, i.e.

$$Co(CN)_5{}^{3-} + RX \xrightarrow{k} Co(CN)_5X^{3-} + R\cdot \quad \text{(rate-determining)} \quad (4)$$

$$Co(CN)_5{}^{3-} + R\cdot \longrightarrow Co(CN)_5R^{3-} \quad \text{(fast)} \quad (5)$$

Evidence for radical intermediates in certain of these reactions has been obtained by Kwiatek and Seyler.[2b] A similar mechanism involving radical intermediates has been proposed for the analogous reactions of chromium(II) with organic halides.[3-5]

Insofar as the data required for this correlation are available or can be inferred, the observed reactivity pattern of Co(CN)₅³⁻ toward different organic halides appears to reflect an inverse dependence on the carbon–halogen bond strength in line with that expected for the proposed mechanism. This is reflected particularly in the pronounced trends, $k_{RCl} < k_{RBr} < k_{RI}$ (k increasing by a factor of 10³–10⁴ for each step of the sequence), and in the trends $k_{X-CH_2CH_2COO^-} < k_{X-CH_2COO^-}$ (by a factor of about 10³), presumably reflecting the weakening of the latter bond owing to resonance stabilization of the resulting free radical. Analogous trends have been observed for the rates of halogen abstraction from organic halides by sodium atoms[12] and by organic free radicals.[13] The increases in k by factors ranging from 30 to 100 in going from X-CH₂COO⁻ to X-CH₂-COOCH₃ or X-CH₂CONH₂ (X = I or Br) are probably due to lowering of the electrostatic repulsion, and the observed accompanying changes in the activation param-

(12) E. Warhurst, *Quart. Rev.* (London), **5**, 44 (1951).
(13) A. F. Trotman-Dickinson, "Free Radicals," Methuen and Co., London, 1959.

Table II. Second-Order Rate Constants for the Reactions of Co(CN)₅³⁻ with Various Organic Halides

Halide	Temp., °C.	k, M^{-1} sec.$^{-1}$ ^{a}
ICH₂COO⁻	5.0	5.0×10^2
	9.8	6.3×10^2
	15.0	6.1×10^2
	21.6	7.3×10^2
	25.0	8.9×10^2
	29.6	8.3×10^2
	33.2	9.2×10^2
ICH₂COOCH₃	9.5	5.2×10^4
	10.5	4.4×10^4
	14.0	7.5×10^4
	20.8	6.6×10^4
	25.0	8.8×10^4
	31.2	9.8×10^4
	34.0	9.8×10^4
ICH₂CONH₂	6.7	1.61×10^4
	13.1	2.01×10^4
	20.8	2.82×10^4
	25.0	2.95×10^4
ICH₂SO₃⁻	10.2	8.8
	20.7	15.5
	25.0	17.6
	31.9	25.1
ICH₂CH₂COO⁻	7.5	0.17
	15.0	0.30
	20.1	0.44
	25.0	0.54
	32.0	0.73
ICH₂CH₂COOCH₃	25.0	$\sim 3^b$
I—⟨○⟩—N (pyridine)	25.0	$\sim 10^{-3\,b}$
I >C=C< COO⁻ / -OOC H	25.0	$\sim 10^{-2\,b}$
BrCH₂COO⁻	25.0	0.28
BrCH₂COOCH₃	25.0	$\sim 34^b$
BrCH₂—⟨○⟩—COO⁻	9.8	61
	19.6	77
	25.0	96
	31.9	105
BrCH₂CONH₂	3.1	5.4
	11.2	8.1
	19.4	12.2
	25.0	16.4
	32.0	22.2
BrC—CBr (meso) H H / -OOC COO⁻	4.8	39
	13.0	54
	20.6	67
	25.0	78
	31.8	97
BrC—CBr (dl) H COO⁻ / -OOC H	4.5	2.7
	13.9	4.1
	20.6	5.7
	32.4	8.4
BrCH₂CH₂COO⁻	25.0	$8 \times 10^{-4\,c}$
BrCHCOO⁻ / CH₃	25.0	$\sim 2^b$
BrCHCOO⁻ / CH₂COO⁻	25.0	0.83
BrCHCOO⁻ / BrCH₂	25.0	11.7
ClCH₂COO⁻	25.0	$\sim 2 \times 10^{-4\,d}$
ClCH₂CONH₂	25.0	$\sim 6 \times 10^{-4\,c}$
ClCH₂COOCH₃	25.0	$\sim 10^{-3\,e}$
ClCHClCOO⁻	25.0	1.9×10^{-2}
	25.0	$4.5 \times 10^{-2\,c}$
ClCCl₂COO⁻ H H	25.0	0.44
ClC—CCl (meso) H H / -OOC COO⁻	25.0	$4.6 \times 10^{-2\,d}$

^{a} Ionic strength, 0.2 M unless otherwise noted. ^{b} Preliminary values. Second-order rate law in these cases not fully established. ^{c} Ionic strength, 1.0 M. ^{d} Ionic strength, 2.0 M. ^{e} Measured in 1:1 methanol–water, by volume.
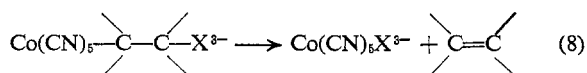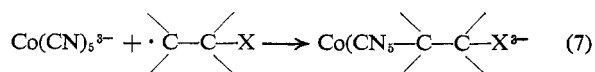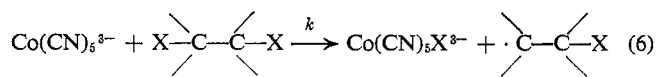
Table III. Activation Parameters for the Reactions of Co(CN)₅³⁻ with Various Organic Halides

Halide	ΔH^*, kcal./mole^a	ΔS^*, e.u.^{b}
ICH₂COO⁻	3.0	−35
ICH₂COOCH₃	4 ± 2	-20 ± 8
ICH₂CONH₂	5.0	−21
ICH₂SO₃⁻	7.7	−27
ICH₂CH₂COO⁻	9.6	−27
BrCH₂—⟨○⟩—COO⁻	3.8	−36
BrCH₂CONH₂	7.5	−27
BrC—CBr (meso) H H / -OOC COO⁻	5.0	−33
BrC—CBr (dl) H COO⁻ / -OOC H	6.2	−34

^{a} Estimated precision ±0.3 kcal./mole except where otherwise noted. ^{b} Estimated precision ±1 e.u. except where otherwise noted.

eters are in line with this. Other noteworthy trends (also paralleled by the rates of halogen abstraction by sodium atoms) are the increases in reactivity along the sequence X–CH₂R < X–CHR₂ and along the sequence ClCH₂R < Cl₂CHR < Cl₃CR.

The reactions of the vicinal dihalides (α,β-dibromosuccinate and α,β-dibromopropionate) followed a somewhat different course as previously noted (and as also previously observed for ethylene dibromide by Kwiatek and Seyler²ᵇ), the stoichiometry in these cases being given by eq. 2. The disappearance of Co(CN)₅³⁻ for this reaction followed at 960 mμ still obeyed the second-order rate law (eq. 3) yielding the values of k given in Table II. However, the appearance of Co(CN)₅Br³⁻ followed at 395 mμ, exhibited more complex kinetic behavior, corresponding to a stepwise process. In the case of the reaction of Co-(CN)₅³⁻ with meso-α,β-dibromosuccinate, formation of Co(CN)₅Br³⁻ appeared to occur by two separate processes, the first coincident with the disappearance of Co-(CN)₅³⁻ and the second involving a subsequent slower reaction having a first-order rate constant of 0.13 sec.⁻¹, which was independent of the concentration of dibromosuccinate. The behavior for dl-α,β-dibromosuccinate and α,β-dibromopropionate appeared to be qualitatively similar although the two paths of formation of Co-(CN)₅Br³⁻ were more difficult to resolve in these cases because of overlapping rates. These observations point to the following stepwise mechanism (eq. 6–8) similar to

$$Co(CN)_5{}^{3-} + X-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \xrightarrow{k} Co(CN)_5X^{3-} + \cdot\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \quad (6)$$

$$Co(CN)_5{}^{3-} + \cdot\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X \longrightarrow Co(CN_5-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X^{3-} \quad (7)$$

$$Co(CN)_5-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X^{3-} \longrightarrow Co(CN)_5X^{3-} + \overset{|}{C}=\overset{|}{C} \quad (8)$$

that suggested by Kray and Castro[4] for the analogous reactions of chromium(II) with vicinal dihalides. The higher rates observed for the vicinal dibromides com-pared with monobromosuccinate are in line with similar differences found in the corresponding reactions of chromium(II).[4] No explanation is available for the markedly higher reactivity of *meso*-α,β-dibromosuccinate compared to the *dl* isomer, reflected in a difference of about 1.2 kcal./mole in ΔH^*.

Deprotonation of Tris(ethylenediamine)rhodium(III) Iodide with Potassium Amide in Liquid Ammonia[1,2]

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The interaction of tris(ethylenediamine)rhodium(III) iodide and potassium amide in liquid ammonia provides products in which protons are sequentially removed from the ligands. Of these, [Rh(en-H)(en)₂]I₂ was isolated at $-70°$, and [Rh(en-H)₂(en)]I and [Rh(en-H)₃] were isolated at $-33.5°$. The infrared spectra of these and the parent complex were studied to examine the effect of deprotonation upon the nature of the metal ion–ligand bond.

It is well established that ligands such as ethylene-diamine and diethylenetriamine are sufficiently acidic to permit deprotonation in appreciably basic media.[3–5] Only little information, however, is thus far available as to the effect of deprotonation upon the nature of the interaction between the central metal ion and the ligand nitrogen atoms. It may be postulated that deprotonation should result in a drift of charge from the nitrogen atom toward the metal ion, thus increasing the bond order.

A comparison of the reactions of ethylenediamine complexes of Pt^{2+}, Pd^{2+}, Ir^{3+}, and Os^{3+} with solutions of potassium amide in liquid ammonia indicates that the acidic properties of the ethylenediamine ligands are enhanced by a high charge and small size of the central metal ion. The Rh^{3+} cation affords a case in which the acidity of the ethylenediamine ligand is greater than in most of the other cases heretofore studied. Ac-cordingly, a greater number of protons should be re-movable from the ethylenediamine ligands associated with Rh^{3+}.

Since studies of the ultraviolet and visible spectra of complexes of this type have been impeded by the lack of a solvent, it was decided to investigate the infrared spectra of the solids isolated as described herein for clues to the nature of the bonding involved. Specifically, shifts in positions of infrared absorption bands should indicate changes in energy for significant atomic vibrational motions.

Experimental Section

The equipment and procedures for reactions in liquid ammonia were the same as described elsewhere.[6]

Rhodium was determined by reduction to the metal in a hydrogen atmosphere at 750°. Iodine was deter-mined by the method of Kolthoff and Stenger.[7] Carbon and hydrogen determinations were performed with a Coleman Model 33 carbon–hydrogen analyzer; and nitrogen was determined with a Coleman Model 29 nitrogen analyzer.

Infrared spectra were obtained with a Beckman IR-7 with CsI interchange optics. Spectra in the re-gion from 700 to 4000 cm.$^{-1}$ were taken as mulls in Nujol or perfluorokerosene on NaCl plates. Spectra in the 200- to 700-cm.$^{-1}$ region were taken as Nujol mulls on either CsBr plates or strips of Handi-Wrap.

Tris(ethylenediamine)rhodium(III) Iodide. The methods for preparation of $[Rh(en)_3]^{3+}$ salts reported by Werner[8] and Jaeger[9] gave products that were of low

(1) This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

(2) The notation (en-H) indicates an ethylenediamine ligand from which a proton has been abstracted.

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