The Reactions of Pentacyanocobaltate(II) with Some Organic Halides[1]

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Abstract: The stoichiometries and kinetics of the reactions of pentacyanocobaltate(II) with a number of alkyl and benzyl halides, as well as with a number of dihalides of the type $X(CH_2)_nX$, were examined in 20 vol % water–80 vol % methanol. The stoichiometries of the reactions with the methyl and benzyl halides (RX) conform to: $2Co(CN)_5{}^{3-} + RX \rightarrow Co(CN)_5R^{3-} + Co(CN)_5X^{3-}$. For CH_3CH_2I, $(CH_3)_2CHI$, and $(CH_3)_3CI$, additional paths exemplified by $2Co(CN)_5{}^{3-} + CH_3CH_2I \rightarrow Co(CN)_5I^{3-} + Co(CN)_5H^{3-} + CH_2{=}CH_2$ were observed. The reactions with ICH_2CH_2I and $ICH_2CH_2CH_2I$ exhibited the stoichiometries $2Co(CN)_5{}^{3-} + ICH_2CH_2I \rightarrow 2Co(CN)_5I^{3-} + CH_2{=}CH_2$ and $2Co(CN)_5{}^{3-} + ICH_2CH_2CH_2I \rightarrow 2Co(CN)_5I^{3-}$ + cyclopropane, respectively. All the reactions exhibited second-order kinetics according to the rate law $-d[Co(CN)_5{}^{3-}]/dt = 2k[Co(CN)_5{}^{3-}][RX]$. The reactivities of the monohalides decreased in the order (values of k at 25° in M^{-1} sec^{-1} in parentheses): $C_6H_5CH_2I$ (3.8×10^3) > $(CH_3)_3CI$ (9.1) > $(CH_3)_2CHI$ (1.20) > CH_3CH_2I (5.9×10^{-2}) > $CH_3CH_2CH_2I$ (4.3×10^{-2}) > CH_3I (9.5×10^{-3}); also $C_6H_5CH_2I$ (3.8×10^3) > p-$NO_2C_6H_4CH_2Br$ (1.05×10^2) > p-$BrC_6H_4CH_2Br$ (7.5) > $C_6H_5CH_2Br$ (2.33) > $C_6H_5CH_2Cl$ (4.9×10^{-4}). The reactivities of the dihalides decreased in the order: $I(CH_2)_2I$ (63) > $I(CH_2)_3I$ (0.99) > $I(CH_2)_3Br$ (0.68) > $I(CH_2)_4I$ (0.30) > $I(CH_2)_5I$ (0.12). The results are interpreted in terms of mechanisms in which the rate-determining step, in each case, is the abstraction of a halogen atom by $Co(CN)_5{}^{3-}$, *i.e.*, $Co(CN)_5{}^{3-} + RX \rightarrow Co(CN)_5X^{3-} + R\cdot$, followed by capture of the radical $R\cdot$ by $Co(CN)_5{}^{3-}$ to form $Co(CN)_5R^{3-}$ (which may undergo subsequent elimination) or by hydrogen abstraction to form $Co(CN)_5H^{3-}$ + olefin. The observed reactivity patterns are compared with those for halogen abstraction from organic halides by methyl radicals and by sodium atoms.

The formation of organocobalt compounds by the reaction, depicted by eq 1, of pentacyanocobaltate(II) with a wide variety of organic halides (RX = CH_3I, $C_6H_5CH_2Br$, $BrCH_2COO^-$, etc.) has previously been described.[2-6] The results of kinetic and other studies of such reactions have been interpreted[3-6] in terms of free-radical mechanisms, depicted by eq 2 and 3, involving halogen atom abstraction by $Co(CN)_5{}^{3-}$ in the rate-determining step.

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

$$Co(CN)_5{}^{3-} + RX \longrightarrow Co(CN)_5X^{3-} + R\cdot \qquad (2)$$

$$Co(CN)_5{}^{3-} + R\cdot \longrightarrow Co(CN)_5R^{3-} \qquad (3)$$

The earlier kinetic studies on such reactions were performed in aqueous solution and were confined to water-soluble organic halides such as $BrCH_2COO^-$, $BrCH_2CONH_2$, etc. By using aqueous methanol as the solvent we have been able to extend these kinetic measurements to a variety of alkyl and benzyl halides, including some dihalides. The results of these investigations, which reveal some new reactivity patterns and mechanistic features, are reported and discussed in this paper. One objective of the work, which was realized, was to compare the rates of halogen abstraction by $Co(CN)_5{}^{3-}$ from a series of organic halides with the corresponding rates of halogen abstraction by other species, notably methyl radicals and sodium atoms.

Experimental Section

Materials. The organic halides were purified by the following procedures. Methyl iodide and ethyl iodide were shaken with a dilute aqueous solution of sodium thiosulfate to remove iodine, then dried over molecular sieves, and distilled in the dark, bp 42–43 and 71–72°, respectively. 1-Iodopropane and 2-iodopropane were redistilled at atmospheric pressures, bp 102–103 and 90–91°, respectively. 2-Iodo-2-methylpropane (bp 35–36°, 90 mm), 1,3-diiodopropane (bp 125°, 50 mm), and α-bromotoluene (bp 127–128°, 80 mm) were distilled under reduced pressure. α-Iodotoluene, 1,2-diiodoethane, α,4-dibromotoluene, and α-bromo-4-nitrotoluene were recrystallized at least twice from ether at low temperatures. 1-Bromo-3-iodopropane[7] was prepared by allowing 1,3-dibromopropane to react in solution with a stoichiometric amount of sodium iodide. Its purity was confirmed by vpc and mass spectral analysis.

Sodium perchlorate (G. F. Smith) was recrystallized three times from distilled water. All other reagents, including the methanol used as solvent, were reagent grade chemicals.

Identification of Products. $Co(CN)_5I^{3-}$ was identified, and its yield determined spectrophotometrically utilizing the characteristic absorption band at 4950 Å (ϵ 117). The volatile organic products were identified, and their yields determined by vpc or, in some cases, by nmr. An Aerograph 660 gas chromatograph, equipped with a hydrogen flame detector and a Sargent SR recorder, was used for the vpc measurements. The column was either a 10-ft 20% Carbowax 400 on 60–80 Chrom P or an 8-ft Poropak Q.

Ultraviolet, visible, and near-infrared spectra were determined with a Cary 14 spectrophotometer and nmr spectra with a Varian A-60 spectrometer.

Kinetic Measurements. The same procedures as described[3] for earlier kinetic measurements on the reactions of $Co(CN)_5{}^{3-}$ with organic halides were employed in the present studies. Reactions with half-lives greater than 10 sec were followed conventionally in a Cary 14 spectrophotometer and those with shorter half-lives in the stopped-flow apparatus. In each case the rate of reac-

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

(3) J. Halpern and J. P. Maher, *ibid.*, **87**, 5361 (1965).

(4) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

(5) J. Kwiatek and J. K. Seyler, Advances in Chemistry Series, No. 70, American Chemical Society, Washington, D. C., 1968, p 207.

(6) J. Kwiatek, *Catalysis Rev.*, **1**, 37 (1967).

(7) Kindly prepared and supplied to us by Professor L. Kaplan, Department of Chemistry, University of Chicago.

Table I. Stoichiometry of the Reactions of $Co(CN)_5^{3-}$ with Organic Monohalides

	Initial reactant concentrations, *M*		Product yields,[a] *M*	
Organic halide	$[Co(CN)_5^{3-}]$	[Organic halide]	$[Co(CN)_5I^{3-}]$	Organic products
CH_3I	9.0×10^{-4}	1.2×10^{-2}	4.3×10^{-4}	None detected
CH_3CH_2I	1.0×10^{-3}	2.1×10^{-2}	5.1×10^{-4}	1.2×10^{-4} $(1.2 \times 10^{-4})^b$ $CH_2{=}CH_2$
				1.0×10^{-4} $(1.3 \times 10^{-4})^b$ CH_3CH_3
$CH_3CH_2CH_2I$	1.1×10^{-3}	4.5×10^{-2}	5.4×10^{-4}	4.1×10^{-4} $(4.1 \times 10^{-4})^c$ $CH_3CH{=}CH_2$
				1.9×10^{-4} $(4.3 \times 10^{-4})^c$ $CH_3CH_2CH_3$
$(CH_3)_2CHI$	1.1×10^{-3}	6.7×10^{-2}	5.4×10^{-4}	5.6×10^{-4} $(5.7 \times 10^{-4})^e$ $CH_3CH{=}CH_2$
			$(7.2 \times 10^{-4})^d$	7.0×10^{-5} $(4.3 \times 10^{-4})^e$ $CH_3CH_2CH_3$
$(CH_3)_3CI$	4.0×10^{-4}	3.3×10^{-3}	...	$(CH_3)_2C{=}CH_2 + (CH_3)_3CH$
$C_6H_5CH_2I$	1.1×10^{-3}	3.1×10^{-3}	5.9×10^{-4}	None detected

[a] Unless otherwise specified, $Co(CN)_5I^{3-}$ was determined immediately following consumption of $Co(CN)_5^{3-}$, and the organic products were determined about 20 min later. [b] After 3 hr. [c] After 5 hr. [d] After 1.5 hr beyond reaction of all the $Co(CN)_5^{3-}$. Some conversion of $Co(CN)_5I^{3-}$ to $Co(CN)_5OH_2^{2-}$ or $Co(CN)_6^{3-}$ had probably occurred during this period. [e] After 10 hr.

tion was measured by following the decrease in the absorbance of $Co(CN)_5^{3-}$ at 9670 Å (ϵ 298). In the case of the reactions with organic iodides, the appearance of $Co(CN)_5I^{3-}$ was also sometimes monitored at 4950 Å (ϵ 117). The two rate measurements always agreed well.

Solvolysis of the organic halide was minimized by introducing it into the reaction solution immediately prior to the experiment. Hydrolysis of $Co(CN)_5I^{3-}$ was sufficiently slow to be neglected. The decomposition of $Co(CN)_5^{3-}$ by reaction with the solvent (to form $Co(CN)_5OH^{3-}$ and $Co(CN)_5H^{3-}$),[8] while apparently faster in the mixed solvent than in water, was sufficiently slow so as not to interfere with any but the slowest reactions investigated, notably those with CH_3I and $C_6H_5CH_2Cl$. In these cases some interference from the decomposition reaction was encountered during the initial stages of the reaction with the organic halide, but beyond the first 30% or so the reaction appeared to be free from such interference. The ratio of total CN^- to Co^{2+} in the solution was generally close to (*i.e.*, 4.8–5.0) the stoichiometric value for the formation of $Co(CN)_5^{3-}$. Excess CN^- was avoided in order to minimize the reaction of CN^- with $Co(CN)_5I^{3-}$ to form $Co(CN)_6^{3-}$.[9]

All the kinetic measurements were made at 25.0 ± 0.2° in 20 vol % water–80 vol % methanol as solvent. The pH, adjusted by addition of NaOH, was generally about 11 or slightly higher. The ionic strength was maintained at 0.02 *M* with sodium perchlorate.

Results and Discussion

Stoichiometry and Products. Most of the reactions examined were between $Co(CN)_5^{3-}$ and organic iodides. The principal questions involved in defining the stoichiometries of these reactions relate to (i) the yield of $Co(CN)_5I^{3-}$, (ii) the nature and yields of organic products, and (iii) the yields of the organocobalt complexes, $Co(CN)_5R^{3-}$, and of the hydrido complex, $Co(CN)_5H^{3-}$.

As described earlier the yield of $Co(CN)_5I^{3-}$, in each case, was determined spectrophotometrically, while the organic products were identified, and their yields determined, by vpc or nmr. Because of the inapplicability of spectrophotometric procedures and the inefficiency of isolation procedures,[2–4] it proved impossible to determine quantitatively the yields of the organo and hydrido complexes. However, in most cases these could be inferred with considerable confidence from the other product determinations, coupled with the results of earlier studies[2–4] in which the stoichiometries of some of the reactions were established.

Monohalides. The results of measurements pertinent to establishing the stoichiometries of the reactions of $Co(CN)_5^{3-}$ with the monoiodides are summarized in Table I. A general feature of these results is that in each case the *initial* yield of $Co(CN)_5I^{3-}$ (when the organic iodide is in excess) is close to one-half the initial concentration of $Co(CN)_5^{3-}$, in accord with the stoichiometry described by eq 1. Variations in the over-all stoichiometry are indicated, however, by the observed organic products. These are most conveniently considered by dividing the reactions into the several classes described below.

(i) CH_3I and $C_6H_5CH_2I$. The reactions of these compounds are characterized by the absence of any organic products. This result and the observed yields of $Co(CN)_5I^{3-}$ are consistent with earlier demonstrations[2] that the stoichiometries of these reactions conform to eq 1.

(ii) $(CH_3)_2CHI$ and $(CH_3)_3CI$. The reaction of $Co(CN)_5^{3-}$ with $(CH_3)_2CHI$ has previously been examined by Kwiatek and Seyler,[5] who postulated the sequence of reactions depicted by eq 4 and 5 to account for the overall stoichiometry, observed by them, which is described by eq 6. Our results are consistent with

$$2Co(CN)_5^{3-} + (CH_3)_2CHI \longrightarrow Co(CN)_5I^{3-} + Co(CN)_5H^{3-} + CH_3CH{=}CH_2 \quad 4)$$

$$Co(CN)_5H^{3-} + (CH_3)_2CHI \longrightarrow Co(CN)_5I^{3-} + (CH_3)_2CH_2 \quad (5)$$

$$2Co(CN)_5^{3-} + 2(CH_3)_2CHI \longrightarrow 2Co(CN)_5I^{3-} + CH_3CH{=}CH_2 + (CH_3)_2CH_2 \quad (6)$$

these observations and conclusions but indicate that reaction 5 (*i.e.*, formation of $(CH_3)_2CH_2$) is relatively slow compared to reaction 4. It has been suggested,[5] and supported by preliminary kinetic observations,[10] that reaction 5 proceeds through the $Co(CN)_5^{3-}$-catalyzed radical mechanism depicted by eq 7 and 8.

$$Co(CN)_5^{3-} + (CH_3)_2CHI \longrightarrow Co(CN)_5I^{3-} (CH_3)_2\dot{C}H \quad (7)$$

$$(CH_3)_2\dot{C}H + Co(CN)_5H^{3-} \longrightarrow (CH_3)_2CH_2 + Co(CN)_5^{3-} \quad (8)$$

Because of the instability of $(CH_3)_3CI$ (due to rapid hydrolysis under the conditions of our reaction), the stoichiometry of the reaction with $Co(CN)_5^{3-}$ could not be established quantitatively. However, in agreement with earlier observations,[6] $(CH_3)_2C{=}CH_2$ and $(CH_3)_3CH$ were found as products and it seems likely that the stoichiometry parallels that for the reaction of $(CH_3)_2CHI$ with $Co(CN)_5^{3-}$.

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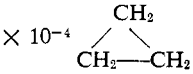
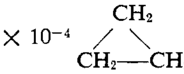
(8) B. de Vries, *J. Catalysis*, **1**, 489 (1962).

(9) J. P. Birk and J. Halpern, *J. Am. Chem. Soc.*, **90**, 305 (1968).

(10) J. Halpern and N. P. Johnson, unpublished results.

Table II. Stoichiometry of the Reactions of $Co(CN)_5^{3-}$ with Organic Dihalides

	Initial reactant concentrations, *M*		Product yields,[a] *M*	
Organic halide	$[Co(CN)_5^{3-}]$	[Organic halide]	$[Co(CN)_5I^{3-}]$	Organic products
$I(CH_2)_2I$	1.1×10^{-3}	3.0×10^{-1}	1.1×10^{-3}	5.8×10^{-4} $CH_2{=}CH_2$
$I(CH_2)_3I$	1.6×10^{-3}	5.4×10^{-3}	1.6×10^{-3}	8.0×10^{-4}  Trace $CH_3CH{=}CH_2$
$I(CH_2)_3Br$	1.6×10^{-3}	3.2×10^{-2}	7.4×10^{-4}	7.4×10^{-4} 
$I(CH_2)_4I$	1.1×10^{-3}	4.7×10^{-2}	6.7×10^{-4}	2.1×10^{-4} $(3.7 \times 10^{-4})^b$ $CH_2{=}CHCH_2CH_3$ 8.0×10^{-5} $(8.8 \times 10^{-5})^b$ *trans*-$CH_3CH{=}CHCH_3$ $(2.9 \times 10^{-5})^b$ *cis*-$CH_3CH{=}CHCH_3$
$I(CH_2)_5I$	1.1×10^{-3}	3.1×10^{-2}	6.1×10^{-4}	$(4.2 \times 10^{-4})^b$ $CH_2{=}CHCH_2CH_2CH_3$ $(2.9 \times 10^{-5})^b$ *cis*-$CH_3CH{=}CHCH_2CH_3$

[a] Unless otherwise stated, $Co(CN)_5I^{3-}$ was determined immediately following consumption of the $Co(CN)_5^{3-}$ and the organic products were determined about 20 min later. [b] After 5 hr.

(iii) CH_3CH_2I and $CH_3CH_2CH_2I$. The over-all stoichiometries of the reactions of $Co(CN)_5^{3-}$ with these substrates can be accounted for in terms of simultaneous reaction paths (depicted by eq 9 and 10) analogous to those described above for CH_3I and $(CH_3)_2CHI$, respectively, *i.e.*

$$2Co(CN)_5^{3-} + CH_3CH_2I \longrightarrow Co(CN)_5I^{3-} + Co(CN)_5CH_2CH_3^{3-} \quad (9)$$

$$2Co(CN)_5^{3-} + 2CH_3CH_2I \longrightarrow 2Co(CN)_5I^{3-} + CH_2{=}CH_2 + CH_3CH_3 \quad (10)$$

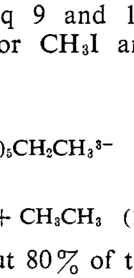
The product analysis indicates that about 80% of the $Co(CN)_5^{3-}$ initially present reacts according to path 9 and about 20% according to path 10.

The stoichiometry of the reaction of $CH_3CH_2CH_2I$ appears to be similar to that of CH_3CH_2I except that the yields of organic products (*i.e.*, the operation of paths analogous to 4 and 5) are somewhat higher.

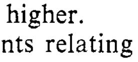
Dihalides. The results of measurements relating to the reactions of $Co(CN)_5^{3-}$ with the organic dihalides are summarized in Table II. The stoichiometries of the reactions with $I(CH_2)_2I$, $I(CH_2)_3I$,[11] and $I(CH_2)_3Br$ are clearly in accord with eq 11–13. The formation of cyclopropane in the reaction of $Co(CN)_5^{3-}$ with $I(CH_2)_3I$ was accompanied by the formation of a trace of propylene when the organic iodide was in excess but not when $Co(CN)_5^{3-}$ was in excess. No propylene could be detected in the reaction with $I(CH_2)_3Br$.

$$2Co(CN)_5^{3-} + I(CH_2)_2I \longrightarrow 2Co(CN)_5I^{3-} + CH_2{=}CH_2 \quad (11)$$

$$2Co(CN)_5^{3-} + I(CH_2)_3I \longrightarrow$$

$2Co(CN)_5I^{3-}$ +  (12)

$$2Co(CN)_5^{3-} + I(CH_2)_3Br \longrightarrow$$

$Co(CN)_5I^{3-} + Co(CN)_5Br^{3-}$ +  (13)

The stoichiometries of the reactions of $Co(CN)_5^{3-}$ with $I(CH_2)_4I$ and $I(CH_2)_5I$ are less well defined. The principal initial products appear to be $Co(CN)_5I^{3-}$ and, presumably, $Co(CN)_5CH_2(CH_2)_2CH_2I^{3-}$ (or $Co(CN)_5CH_2(CH_2)_3CH_2I^{3-}$), accompanied by the formation of some olefin products, the yield of which increases on standing. Significantly, no cyclobutane or cyclopentane could be detected, either by vpc or nmr.

Kinetics and Mechanisms. 1. Monohalides. The reaction of $Co(CN)_5^{3-}$ with each of the monohalides examined exhibited simple second-order kinetics, first order in each of the reactants, in accord with the rate law defined by eq 14. Under the conditions of our rate measurements, with the organic halide (whose concentration was varied within the range 1×10^{-3} to 0.25 *M*) always in at least tenfold excess over $Co(CN)_5^{3-}$ (whose initial concentration was generally in the range 10^{-4} to 10^{-3} *M*), the observed kinetics were pseudo first order, *i.e.*

$$-d[Co(CN)_5^{3-}]/dt = 2k[Co(CN)_5^{3-}][RX] \quad (14)$$

$$-d \ln [Co(CN)_5^{3-}]/dt = k_{obsd} = 2k[RX] \quad (15)$$

Values of k_{obsd}, determined from the slopes of first-order kinetic plots, together with the corresponding values of k computed from eq 15, are listed in Table III.

The reactions of $Co(CN)_5^{3-}$ with methyl iodide and with the benzyl halides, the stoichiometries of which are in accord with eq 1, are most readily accommodated by the simple free-radical mechanism (eq 16 and 17) previously proposed,[3,4] in which the rate-determining step involves the abstraction of a halogen atom by $Co(CN)_5^{3-}$, *i.e.*

$$Co(CN)_5^{3-} + RX \xrightarrow{k} Co(CN)_5X^{3-} + R\cdot \quad (16)$$

$$Co(CN)_5^{3-} + R\cdot \longrightarrow Co(CN)_5R^{3-} \quad (17)$$

In addition to the kinetic evidence favoring such a mechanism, direct evidence for the free-radical intermediates has been provided by trapping them with acrylonitrile and with $Co(CN)_5H^{3-}$ (eq 7 and 8).[5,6]

The reactions of $Co(CN)_5^{3-}$ with CH_3CH_2I, $(CH_3)_2CHI$, and $(CH_3)_3CI$ are most readily interpreted in terms of related mechanisms, also involving halogen atom abstraction as the rate-determining step, but with competition between alternative subsequent reactions (combination *vs.* H atom abstraction) between Co-

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[11] The formation of cyclopropane by reaction of $Co(CN)_5^{3-}$ with $ICH_2CH_2CH_2I$ has previously been reported by Kwiatek.[6] Dehalogenation of 1,3-dihalopropanes by chromium(II) (J. K. Kochi, *Rec. Chem. Progr.*, **27**, 207 (1966)) and by bis(dimethylglyoximato)cobalt(II) (G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966)) has also been reported to yield cyclopropane.

Table III. Kinetic Data for Monohalides

Organic halide	[Organic halide], M	k_{obsd}, sec^{-1}	k, M^{-1} sec^{-1}
CH_3I	0.86×10^{-1}	1.43×10^{-3}	0.83×10^{-2}
	1.24×10^{-1}	2.53×10^{-3}	1.02×10^{-2}
	1.61×10^{-1}	2.68×10^{-3}	0.83×10^{-2}
	1.98×10^{-1}	4.21×10^{-3}	1.04×10^{-2}
	2.48×10^{-1}	5.07×10^{-3}	1.02×10^{-2}
			$k_{\mathrm{av}} = (0.95 \pm 0.1) \times 10^{-2}$
CH_3CH_2I	1.09×10^{-2}	1.50×10^{-3}	6.9×10^{-2}
	3.07×10^{-2}	3.67×10^{-3}	6.0×10^{-2}
	3.86×10^{-2}	4.92×10^{-3}	6.4×10^{-2}
	4.20×10^{-2}	4.37×10^{-3}	5.5×10^{-2}
	5.01×10^{-2}	5.63×10^{-3}	5.6×10^{-2}
	5.46×10^{-2}	6.10×10^{-3}	5.6×10^{-2}
			$k_{\mathrm{av}} = (5.9 \pm 0.5) \times 10^{-2}$
$CH_3CH_2CH_2I$	1.02×10^{-2}	0.93×10^{-3}	4.6×10^{-2}
	1.31×10^{-2}	1.16×10^{-3}	4.4×10^{-2}
	1.54×10^{-2}	1.28×10^{-3}	4.2×10^{-2}
	2.56×10^{-2}	2.27×10^{-3}	4.4×10^{-2}
	3.59×10^{-2}	3.26×10^{-3}	4.6×10^{-2}
	4.10×10^{-2}	3.13×10^{-3}	3.8×10^{-2}
	5.13×10^{-2}	4.55×10^{-3}	4.4×10^{-2}
			$k_{\mathrm{av}} = (4.3 \pm 0.3) \times 10^{-2}$
$(CH_3)_2CHI$	2.5×10^{-3}	0.61×10^{-2}	1.22
	5.0×10^{-3}	1.22×10^{-2}	1.22
	7.5×10^{-3}	1.75×10^{-2}	1.17
	10.0×10^{-3}	2.35×10^{-2}	1.18
	12.5×10^{-3}	3.01×10^{-2}	1.21
			$k_{\mathrm{av}} = 1.20 \pm 0.03$
$(CH_3)_3CI$	1.34×10^{-3}	2.6×10^{-2}	9.7
	2.00×10^{-3}	3.5×10^{-2}	8.8
	2.67×10^{-3}	5.0×10^{-2}	9.4
	3.34×10^{-3}	6.1×10^{-2}	9.1
			$k_{\mathrm{av}} = 9.1 \pm 0.5$
$C_6H_5CH_2I$	0.84×10^{-3}	6.27	3.7×10^{3}
	1.31×10^{-3}	10.6	4.0×10^{3}
	1.68×10^{-3}	11.5	3.5×10^{3}
	2.52×10^{-3}	18.3	3.6×10^{3}
	3.36×10^{-3}	25.7	3.9×10^{3}
			$k_{\mathrm{av}} = (3.8 \pm 0.2) \times 10^{3}$
$C_6H_5CH_2Br$	3.57×10^{-2}	1.68×10^{-1}	2.35
	4.70×10^{-2}	2.18×10^{-1}	2.32
	5.77×10^{-2}	2.66×10^{-1}	2.32
	6.82×10^{-2}	3.16×10^{-1}	2.31
			$k_{\mathrm{av}} = 2.33 \pm 0.02$
p-$BrC_6H_4CH_2Br$	1.31×10^{-2}	1.87×10^{-1}	7.2
	1.94×10^{-2}	2.72×10^{-1}	7.0
	2.54×10^{-2}	4.10×10^{-1}	8.0
	3.36×10^{-2}	5.17×10^{-1}	7.7
			$k_{\mathrm{av}} = 7.5 \pm 0.5$
p-$NO_2C_6H_4CH_2Br$	0.87×10^{-2}	1.84	1.07×10^{2}
	1.14×10^{-2}	2.37	1.04×10^{2}
	1.40×10^{-2}	3.07	1.10×10^{2}
	1.66	3.21	0.97×10^{2}
			$k_{\mathrm{av}} = (1.05 \pm 0.05) \times 10^{2}$
$C_6H_5CH_2Cl$	0.94×10^{-1}	0.96×10^{-4}	5.1×10^{-4}
	1.56×10^{-1}	1.44×10^{-4}	4.6×10^{-4}
			$k_{\mathrm{av}} = (4.9 \pm 0.3) \times 10^{-4}$

Table IV. Comparison of the Reactivities of $Co(CN)_5^{3-}$, CH_3, and Na toward Various Organic Halides (RX)

		k_{RX}/k_{CH_3X}		
R	k,[a] M^{-1} sec^{-1}	$Co(CN)_5^{3-} + RI \rightarrow Co(CN)_5I^{3-} + R\cdot$	$CH_3 + RI \rightarrow CH_3I + R\cdot$ [b]	$Na + RCl \rightarrow NaCl + R\cdot$ [c]
CH_3	9.5×10^{-3}	1	1	1
CH_3CH_2	5.9×10^{-2}	6.2	4.0	1.4
$CH_3CH_2CH_2$	4.3×10^{-2}	4.5	..	2.3
$(CH_3)_2CH$	1.20	1.3×10^2	19	3.0
$(CH_3)_3C$	9.1	9.5×10^2	37	6.7
$C_6H_5CH_2$	3.8×10^3	4.0×10^5	1.7×10^2	$\sim 1 \times 10^4$

[a] From Table III. [b] Computed from data in ref 12 based on measurements in toluene at 65°. [c] Computed from data in ref 13 based on measurements in the gas phase using the sodium flame technique.

$(CN)_5^{3-}$ and the resulting free radical. Equations 18–20 illustrate this mechanism for CH_3CH_2I. The competition

$$Co(CN)_5^{3-} + CH_3CH_2I \xrightarrow{k} Co(CN)_5I^{3-}\cdot + CH_2CH_2 \quad (18)$$

$$Co(CN)_5^{3-} + CH_3\dot{C}H_2 \begin{array}{l} \xrightarrow{k_C} Co(CN)_5CH_2CH_3^{3-} \quad (19a) \\ \xrightarrow{k_A} Co(CN)_5H^{3-} + CH_2CH_2 \quad (19b) \end{array}$$

$$Co(CN)_5H^{3-} + CH_3CH_2I \xrightarrow{slow} Co(CN)_5I^{3-} + CH_3CH_3 \quad (20)$$

petition between the combination (k_C) and abstraction (k_A) reactions is analogous to that observed in the reaction between ethyl radicals,[12] where the corresponding two paths (combination and disproportionation) yield $CH_3CH_2CH_2CH_3$ and $CH_3CH_3 + CH_2{=}CH_2$, respectively. From the product distribution ($CH_2{=}CH_2$ to $Co(CN)_5I^{3-}$ ratio), the ratio of the rate constants, k_C:k_A, can be deduced to be approximately 4. The fact that the yield of $CH_2{=}CH_2$ does not increase on standing indicates that it is formed directly in accord with the proposed mechanism rather than by elimination from $Co(CN)_5CH_2CH_3^{3-}$. The stability of the latter has also been demonstrated by the isolation of its sodium salt.[2] For $(CH_3)_2CHI$ and $(CH_3)_3CI$, where the initial yield of olefin approaches that of $Co(CN)_5I^{3-}$, abstraction is presumably highly favored over combination (*i.e.*, $k_A \gg k_C$).

One of the objectives of studying the reactions of $Co(CN)_5^{3-}$ with this particular series of organic halides was to compare the relative rates of halogen atom abstraction by $Co(CN)_5^{3-}$ with those for other reagents. The available data which are summarized in Table IV permit such comparison of $Co(CN)_5^{3-}$ with methyl radicals[13] and with sodium atoms.[14] The reactivity sequences, *i.e.*, $C_6H_5CH_2X > (CH_3)_3CX > (CH_3)_2CHX > CH_3CH_2X \approx CH_3CH_2CH_2 > CH_3X$, are seen to be similar for all three reagents and presumably reflect an inverse dependence of the rate of halogen abstraction on the carbon–halogen bond dissociation energy. Two noteworthy points of comparison are (i) the reversal of the reactivity orders of CH_3CH_2I and $CH_3CH_2CH_2I$ in going from Na to $Co(CN)_5^{3-}$, possibly reflecting the greater importance of steric factors in the latter case, and (ii) the somewhat greater spread in the rate constants for $Co(CN)_5^{3-}$ compared with those for CH_3 and Na. This probably reflects, in part at least, the lower absolute reactivity (and hence greater selectivity) of $Co(CN)_5^{3-}$ compared with the other two species. As the rates of reaction approach the diffusion-controlled limit (as they are known to for Na),[13] the selectivity must become small. Unfortunately the absolute values of the rate constants for the reactions of CH_3 are not known, the relative rates having been determined by a competition method. The similarity of these reactivity patterns emphasizes the free-radical-like reactivity exhibited by $Co(CN)_5^{3-}$ in these and other reactions.[15]

2. Dihalides. The reactions of $Co(CN)_5^{3-}$ with the dihalides also obeyed second-order kinetics similar to those observed for the monohalides. The results of the kinetic measurements on these reactions are summarized in Table V. Despite the differences in stoichiometry among them, it seems likely that for these reactions also the rate-determining step is the abstraction of one I atom by $Co(CN)_5^{3-}$ to form an iodoalkyl radical $ICH_2(CH_2)_{n-2}CH_2$ where n is the number of car-

Table V. Kinetic Data for Dihalides

Organic halide	[Organic halide], M	k_{obsd}, sec^{-1}	k, M^{-1} sec^{-1}
$I(CH_2)_2I$	1.16×10^{-2}	1.40	60
	1.71×10^{-2}	2.26	66
	2.25×10^{-2}	2.68	60
	2.76×10^{-2}	3.40	62
			$k_{av} = 63 \pm 3$
$I(CH_2)_3I$	2.5×10^{-3}	0.50×10^{-2}	1.00
	4.3×10^{-3}	0.85×10^{-2}	0.99
	6.5×10^{-3}	1.28×10^{-2}	0.99
	8.7×10^{-3}	1.69×10^{-2}	0.97
			$k_{av} = 0.99 \pm 0.02$
$I(CH_2)_3Br$	2.8×10^{-3}	0.39×10^{-2}	0.71
	4.6×10^{-3}	0.56×10^{-2}	0.61
	6.9×10^{-3}	0.89×10^{-2}	0.65
	9.2×10^{-3}	1.22×10^{-2}	0.66
			$k_{av} = 0.68 \pm 0.03$
$Br(CH_2)_3Br$	3.4×10^{-2}	Too slow to measure	
$I(CH_2)_4I$	2.9×10^{-3}	1.7×10^{-3}	0.29
	5.7×10^{-3}	3.6×10^{-3}	0.32
	8.6×10^{-3}	4.9×10^{-3}	0.29
	10.8×10^{-3}	6.1×10^{-3}	0.28
			$k_{av} = 0.30 \pm 0.02$
$I(CH_2)_5I$	0.50×10^{-2}	1.32×10^{-3}	0.13
	1.01×10^{-2}	2.6×10^{-3}	0.13
	1.52×10^{-2}	3.4×10^{-3}	0.11
	2.03×10^{-2}	5.3×10^{-3}	0.13
			$k_{av} = 0.12 \pm 0.01$

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(12) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 107 (1961).

(13) R. J. Fox, F. W. Evans, and M. Szwarc, *Trans. Faraday Soc.*, **57**, 1915 (1961).

(14) H. V. Hartel and M. Polanyi, *Z. Physik. Chem.*, **B19**, 139 (1932).

(15) J. Halpern, ref 5, p 1.

bon atoms separating the two halogen atoms. Differences in the subsequent reactions of these radicals then account for the different observed stoichiometries.

For the reaction of $Co(CN)_5^{3-}$ with ICH_2CH_2I, the following mechanism, analogous to that previously proposed for the reaction of $Co(CN)_5^{3-}$ with α,β-dibromosuccinate (to yield $2Co(CN)_5Br^{3-}$ and fumarate) seems likely.

$$Co(CN)_5^{3-} + ICH_2CH_2I \xrightarrow{k} Co(CN)_5I^{3-} + ICH_2\dot{C}H_2 \quad (21)$$

$$Co(CN)_5^{3-}\ ICH_2\dot{C}H_2 \longrightarrow Co(CN)_5CH_2CH_2I^{3-} \quad (22)$$

$$Co(CN)_5CH_2CH_2I^{3-} \longrightarrow Co(CN)_5I^{3-} + CH_2{=}CH_2 \quad (23)$$

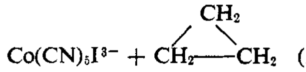
While no direct evidence is available in this case for the discrete olefin elimination step depicted by eq 23, such a step has been directly observed in the corresponding reaction of $Co(CN)_5^{3-}$ with α,β-dibromosuccinate.[3] Analogous mechanisms have also been postulated for the reaction of chromium(II) with vicinal dihalides.[16]

In the case of the reaction of $Co(CN)_5^{3-}$ with $ICH_2CH_2CH_2I$ (eq 12), direct evidence for a stepwise mechanism is provided by the observation that, at sufficiently high $ICH_2CH_2CH_2I$ concentrations ($>2 \times 10^{-2}$ *M*), the formation of $Co(CN)_5I^{3-}$ occurs in two distinct stages. The formation of one-half of the $Co(CN)_5I^{3-}$ coincides with the disappearance of $Co(CN)_5^{3-}$, whereas the other half is produced in a subsequent slower step involving the first-order decomposition of an intermediate. These observations point to a mechanism, depicted by eq 24–26, analogous to that postulated above for the reaction with ICH_2CH_2I, *i.e.*

$$Co(CN)_5^{3-} + ICH_2CH_2CH_2I \xrightarrow{k} Co(CN)_5I^{3-} + ICH_2CH_2\dot{C}H_2 \quad (24)$$

$$Co(CN)_5^{3-} + ICH_2CH_2\dot{C}H_2 \longrightarrow Co(CN)_5CH_2CH_2CH_2I^{3-} \quad (25)$$

$$Co(CN)_5CH_2CH_2CH_2I^{3-} \xrightarrow{k'}$$



$$Co(CN)_5I^{3-} + \overset{CH_2}{CH_2\!-\!CH_2} \quad (26)$$

Direct observation of the last step yields a value of 3.6 $\times$ 10^{-3} sec^{-1} for k'. Similarly in the reaction of $Co(CN)_5^{3-}$ with $ICH_2CH_2CH_2Br$ (eq 13), the formation of $Co(CN)_5I^{3-}$ was found to coincide with the disappearance of $Co(CN)_5^{3-}$ ($k = 0.66$ M^{-1} sec^{-1}) while the formation of $Co(CN)_5Br^{3-}$ occurred in a subsequent step involving the first-order ($k' = 3.6 \times 10^{-3}$ sec^{-1}) decomposition of an intermediate, presumably $Co(CN)_5CH_2CH_2CH_2Br^{3-}$.

The traces of proplyene which were found to accompany the formation of cyclopropane in the reaction of $Co(CN)_5^{3-}$ with $ICH_2CH_2CH_2I$, *when $Co(CN)_5^{3-}$ was in excess*, are attributed to a competing reaction path (eq 27 and 28) involving I atom abstraction by $Co(CN)_5^{3-}$ from the intermediate $Co(CN)_5CH_2CH_2CH_2I^{3-}$, *i.e.*

$$Co(CN)_5CH_2CH_2CH_2I^{3-} + Co(CN)_5^{3-} \longrightarrow Co(CN)_5I^{3-} + Co(CN)_5CH_2CH_2CH_2^{3-} \quad (27)$$

$$Co(CN)_5CH_2CH_2CH_2^{3-} \longrightarrow Co(CN)_5^{3-} + CH_3CH{=}CH_2 \quad (28)$$

The fact that no propylene was formed in the reaction of $ICH_2CH_2CH_2Br$, even at high $Co(CN)_5^{3-}$ concentrations, is consistent with other observations (see Table III and ref 3) that Br abstraction by $Co(CN)_5^{3-}$ (in this case from $Co(CN)_5CH_2CH_2CH_2Br^{3-}$) is generally much slower than I abstraction.

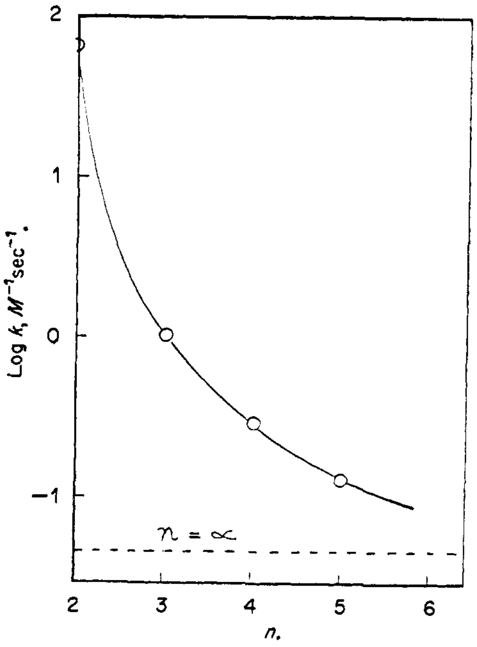


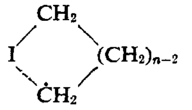
Figure 1. Dependence of the rate constant for the reaction of $Co(CN)_5^{3-}$ with $I(CH_2)_nI$ on n. The dotted line designated $n = \alpha$ denotes the rate constant for the reaction of $Co(CN)_5^{3-}$ with $CH_3CH_2CH_2I$.

The observed products of the reactions of $Co(CN)_5^{3-}$ with $ICH_2(CH_2)_2CH_2I$ and $ICH_2(CH_2)_3CH_2I$ suggest that the principal contributions in these cases arise from reaction paths analogous to those characteristic of the monohalides, *i.e.*

$$2Co(CN)_5^{3-} + ICH_2(CH_2)_{n-2}CH_2I \longrightarrow Co(CN)_5I^{3-} + Co(CN)_5CH_2(CH_2)_{n-2}CH_2I^{3-} \quad (29)$$

The yield of $Co(CN)_5I^{3-}$ in these cases is only slightly in excess of that predicted by eq 29, and no cyclic products are detected. Some olefin formation is, however, observed in these reactions (Table II), the yield of which increases on standing suggesting that the olefins result from the decomposition of the iodoalkylcobalt complexes, $Co(CN)_5CH_2(CH_2)_{n-2}CH_2I^{3-}$.

Finally, an important feature of these results involves the observation that the rate constants (k) for the reactions of $Co(CN)_5^{3-}$ with the diiodides are higher than with corresponding monoiodides such as CH_3CH_2I or $CH_3CH_2CH_2I$. The value of k exhibits an inverse dependence, depicted in Figure 1, on n, the number of carbon atoms separating the two iodine atoms. The most probable origin of this enhanced reactivity is considered to be stabilization of the iodoalkyl radical produced by iodine abstraction by the residual iodine substituent, possibly through cyclic bridging, *i.e.*



Such a neighboring group stabilization has previously been invoked to explain the enhanced reactivities of vicinal dihalides, as compared with monohalides, toward

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(16) C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, **85**, 2768 (1963); **86**, 4603 (1964).

$Co(CN)_5^{3-}$ [3] and Cr^{2+}.[16] Other evidence in favor of stabilization of α-bromoalkyl free radicals by cyclic bridging has come from studies on the photobromination of alkyl bromides[17,18] and from esr measurements on such radicals.[19] The slightly lower reactivity of $Co(CN)_5^{3-}$ toward $ICH_2CH_2CH_2Br$ than toward $ICH_2CH_2CH_2I$ is consistent with the expectation that such stabilization should be more effective for I than for Br. While considered less likely than the explanation just offered, an alternative possibility, namely that the enhanced reactivities of the dihalides result, in part at least, from an inductive effect transmitted through the carbon chain, cannot be ruled out.

(17) W. Thaler, *J. Am. Chem. Soc.*, **85**, 2607 (1963).

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Transition Metal Polypyrazolylborates Containing Other Ligands

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Abstract: Tripyrazolylborate ions, $RB(pz)_3^-$, a new class of uninegative tridentate ligands of C_{3v} symmetry, react with group VIb hexacarbonyls yielding anions of structure $RB(pz)_3M(CO)_3^-$ isolable as tetraethylammonium salts. These anions react with allylic halides yielding directly the thermally very stable π-allyl compounds $RB(pz)_3M(CO)_2$-π-C_3H_5, including those with diverse substituents on carbon and boron. The carbonyl stretching frequencies in these compounds reflect the electron-releasing or -withdrawing nature of the substituents. Reaction with alkyl halides and with protonic acids yields the air-sensitive, seven-coordinate species $RB(pz)_3M(CO)_3R'$ and $RB(pz)_3M(CO)_3H$, respectively. The reaction of $B(pz)_4Mo(CO)_3^-$ with $C_7H_7BF_4$ leads to $B(pz)_4Mo(CO)_2$-π-C_7H_7 which, as well as substituted analogs, is also obtained by the reaction of $RB(pz)_3^-$ with $C_7H_7Mo(CO)_2I$. The compound $B(pz)_4Mo(CO)_2$-π-C_5H_5 results from the reaction of $B(pz)_4^-$ with $C_5H_5Mo(CO)_3Cl$. In $B(pz)_4Mo(CO)_2$-π-C_7H_7 and $B(pz)_4Mo(CO)_2$-π-C_5H_5, the $B(pz)_4^-$ ion seems to act as a bidentate ligand. $RB(pz)_3Mn(CO)_3$, $RB(pz)_3Pd$-π-C_3H_5, and $RB(pz)_3Rh(C_2H_4)_2$ have resulted from the nucleophilic reaction of $RB(pz)_3^-$ with the appropriate halogenated precursor. A number of these molecules are stereochemically nonrigid.

The recent discovery[1] of poly(1-pyrazolyl)borate anions, a novel class of chelating ligands, has opened up a new subarea of organometallic chemistry. Numerous four- and six-coordinate transition metal compounds, based on bis- and tris(pyrazolyl)borates, have been prepared.[2] The latter, of essentially D_{3d} symmetry, are exceedingly stable, many being more stable than their metallocene analogs.

The tris(1-pyrazolyl)borate ligand, a uninegative tridentate of C_{3v} (or local C_{3v}) symmetry, may be used to prepare sandwich-like compounds, where the transition metal is surrounded in essentially octahedral fashion by the termini of the two tridentate ligands. Moreover, it is possible to synthesize half-sandwiches[3] where three coordination sites on the metal are taken up by the $RB(pz)_3$ ligand (pz = 1-pyrazolyl group) and the remaining coordination sites by other groups. Since these other ligands may be varied in manifold ways, the scope of half-sandwich chemistry based on the $RB(pz)_3$ ligand ought to considerably exceed that of the corresponding full sandwiches—just as in the case of the C_5H_5 ligand or the more recently discovered carbollide[4] and related ions.[5-7] This is borne out by some recently reported preliminary results.[8] Several features of the $RB(pz)_3$ ligand make it very attractive. (1) The salts, *e.g.*, $KRB(pz)_3$, are easy to prepare and are indefinitely stable to storage in air; furthermore, the cation may be also varied, as needed, for solubility purposes. (2) When C-substituted pyrazoles are used to synthesize the tris(1-pyrazolyl)borate ligand, the C_{3v} symmetry is maintained,[9] and the substituted $RB(pz)_3$ ligand may thus be used to probe the symmetry of other groups bonded to the metal. (3) Up to ten substituents (including R) may be put on the $RB(pz)_3$ ligand enabling one to influence the environment of the transition metal electronically or sterically, yet maintain the basic chelate geometry intact. Such substitution was found to alter dramatically, for instance, the magnetic properties[10] of some transition metal poly(1-pyrazolyl)borates.

This paper reports the synthesis and properties of

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(1) S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966).

(2) S. Trofimenko, *ibid.*, **89**, 3170 (1967).

(3) The term sandwich has been traditionally used to denote transition metal compounds π-bonded to aromatic ligands. While $RB(pz)_3$ is not a π-bonding aromatic ligand, when one regards its chemistry, it is convenient to visualize $RB(pz)_3$ as replacing a C_5H_5 ligand in full or half-sandwiches. It is in this context that the term "sandwich" is used.

(4) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *ibid.*, **90**, 879 (1968).

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(6) W. H. Knoth, *J. Am. Chem. Soc.*, **89**, 3342 (1967).

(7) D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *ibid.*, **89**, 3342 (1967).

(8) S. Trofimenko, *ibid.*, **89**, 3904 (1967).

(9) S. Trofimenko, *ibid.*, **89**, 6288 (1967).

(10) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, **89**, 3158 (1967).