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Reductions of Hexabromoiridate(IV) by Chromium(II) and by Pentacyanocobaltate(II). Evidence for Bromide-Bridged Binuclear Intermediates[1]

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The reaction between hexabromoiridate(IV) and chromium(II) proceeds in two stages and produces, ultimately, $IrBr_6^{3-}$ and $Cr(H_2O)_6^{3+}$ in ~60% yield and $IrBr_5(H_2O)^{2-}$ and $Cr(H_2O)_5Br^{2+}$ in ~40% yield. In the first stage, too fast to be measured ($k > 10^6$ M^{-1} s^{-1}), Ir(IV) and Cr(II) react via parallel inner-sphere and outer-sphere pathways. The outer-sphere reaction yields $IrBr_6^{3-}$ and $Cr(H_2O)_6^{3+}$. The inner-sphere path produces an intermediate identified as the successor complex $Br_5Ir^{III}BrCr^{III}(H_2O)_5$, which decomposes with a rate constant of 0.65 s^{-1} at 25 °C and 1.0 M ionic strength and associated activation parameters $\Delta H^* = 17.0 \pm 0.5$ kcal/mol and $\Delta S^* = -2.4 \pm 1.8$ eu. The binuclear intermediate dissociates via parallel bond-rupture processes. Cr–Br bond rupture yields $IrBr_6^{2-}$ and $Cr(H_2O)_6^{3+}$, whereas Ir–Br bond rupture produces $IrBr_5(H_2O)^{2-}$ and $Cr(H_2O)_5Br^{2+}$. The $Co(CN)_5^{3-}$–$IrBr_6^{2-}$ reaction also proceeds in two stages. The first, too fast to be measured ($k > 10^6$ M^{-1} s^{-1}), corresponds to an inner-sphere reaction and yields an intermediate identified as the successor binuclear complex $Br_5Ir^{III}BrCo^{III}(CN)_5^{5-}$. The intermediate decomposes via parallel Ir–Br and Co–Br bond-rupture processes to produce $IrBr_6^{3-}$ and $Co(CN)_5(H_2O)^{2-}$ in 58% yield and $IrBr_5(H_2O)^{2-}$ and $Co(CN)_5Br^{3-}$ in 42% yield. The rate constant for the decomposition of the intermediate at 25 °C and ionic strength 0.10 M is 5.6 s^{-1} with $\Delta H^* = 14.9 \pm 0.4$ kcal/mol and $\Delta S^* = -5.1 \pm 1.2$ eu. The mechanisms of these reactions are compared with those of the analogous $IrCl_6^{2-}$–Cr^{2+} and $IrCl_6^{2-}$–$Co(CN)_5^{3-}$ reactions.

Detailed investigations of ligand-bridged binuclear intermediates, which persist for some time following an inner-sphere electron-transfer process, have been reported only in few instances. The detection of chloride-bridged successor complexes in the reduction of hexachloroiridate(IV) by chromium(II)[2,3] or pentacyanocobaltate(II)[4] has added to our understanding of the mechanism of oxidation–reduction reactions. In particular, the kinetic and stoichiometric studies of the dissociation of the binuclear complexes have given considerable insight into the factors that govern whether there is net transfer of the bridging ligand from oxidant to reductant in the overall redox reaction. In order to extend the scope of these studies, we have investigated the reduction of hexabromoiridate(IV) by chromium(II) and by pentacyanocobaltate(II).

Experimental Section

Materials. Sodium perchlorate was prepared by neutralization of sodium carbonate with perchloric acid and was recrystallized three times. Chromium(II) perchlorate solutions were prepared by reduction of solutions of chromium(III) perchlorate of known concentration with amalgamated zinc. Pentacyanocobaltate(II) solutions were prepared by addition of cobalt(II) perchlorate solutions to solutions containing the desired amounts of sodium cyanide, sodium hydroxide, and sodium perchlorate. All manipulations with oxygen-sensitive reagents were carried out under an atmosphere of purified argon.[4] Glass syringes and Teflon needles were used for transferring reagents anaerobically.

Samples of K_2IrBr_6 were prepared from $Na_2IrCl_6\cdot6H_2O$ (Alfa Inorganics) and from impure samples of K_2IrBr_6 (Platinum Chemicals). $Na_2IrCl_6\cdot6H_2O$ (1.6 g) was treated with 30 mL of 40% hydrobromic acid and 10 mL of bromine, and the mixture was allowed to reflux for 12–14 h. Most of the hydrobromic acid was neutralized by adding 50% potassium hydroxide, and then 15 mL of a saturated potassium acetate solution was added. The solid obtained was separated by decantation and washed several times with carbon tetrachloride and then with ethanol. The resulting solid was treated with 10 mL of 40% hydrobromic acid and 6 mL of bromine, and the mixture was allowed to reflux for 12–14 h. The fine, dark purple crystals were decanted, washed with carbon tetrachloride and then with ethanol, and finally dried by suction. The same procedure was used when K_2IrBr_6 was used as the starting material, except that the first refluxing was carried out in the presence of 45 mL of water. The equivalent weight of the samples of K_2IrBr_6 used, measured by reaction with excess iodide followed by titration of the triiodide formed with thiosulfate, was 752 ± 1, as compared to 749.9 calculated for pure K_2IrBr_6.

Solutions containing the hexabromoiridate(III) ion were obtained by in situ reduction of $IrBr_6^{2-}$ with the equivalent amount of ascorbic acid.

Kinetic Measurements. For measurements of the $IrBr_6^{2-}$–Cr^{2+} reaction, solutions of $IrBr_6^{2-}$ with the desired amounts of $HClO_4$ and $NaClO_4$ were mixed in a stopped-flow apparatus with solutions of Cr^{2+} containing the same amounts of $NaClO_4$ and $HClO_4$. The disappearance of the intermediate produced was monitored at several wavelengths in the 500–265-nm region, and the absorbance vs. time data, collected in a 1800 IBM computer interfaced to the stopped-flow apparatus, were fitted by a nonlinear least-squares program to eq 1,

$$A_t = A_\infty + (A_0 - A_\infty) \exp(k_{obsd}t) \tag{1}$$

where A_0, A_t, and A_∞ are the absorbances at time 0, t, and after 8–10 half-lives, respectively, and k_{obsd} is the first-order rate constant for the decomposition of the intermediate. The rate constant for the decomposition of the intermediate produced in the $IrBr_6^{2-}$–$Co(CN)_5^{3-}$ reaction was obtained following the procedure outlined above, except that solutions of $IrBr_6^{2-}$ and Co^{2+} with the desired amount of $NaClO_4$ were mixed with solutions of NaCN and NaOH containing the same amount of $NaClO_4$. $Co(CN)_5^{3-}$ was maintained in excess over $IrBr_6^{2-}$ to avoid the slower reduction of $IrBr_6^{2-}$ by cyanide ion.

The rate of aquation of $IrBr_6^{3-}$ (eq 2) was measured spectro-

$$IrBr_6^{3-} + H_2O = IrBr_5OH_2^{2-} + Br^- \tag{2}$$

photometrically using a Cary 14 spectrophotometer. Two different procedures were employed. In the continuous-monitoring procedure, solutions containing the desired amounts of $IrBr_6^{3-}$, $HClO_4$, and $NaClO_4$ were placed in a cell in the thermostated compartment of the spectrophotometer, and the increase in absorbance at 375 or 436

Table I. Electronic Spectra of Bromoiridate Complexes

Complex	λ_{max}, nm	A_M, M^{-1} cm^{-1}
$IrBr_6^{2-}$	696	2.66×10^3
	676	2.71×10^3
	584	3.87×10^3
	547	1.82×10^3
	512	2.26×10^3
$IrBr_5OH_2^-$	675	2.00×10^3
	587	3.32×10^3
$IrBr_6^{3-}$	448	1.65×10^2
	388	1.27×10^2
$IrBr_5OH_2^{2-}$	436	2.09×10^2
	375	1.65×10^2

Table II. Kinetics of Aquation of $IrBr_6^{3-}$ in 1.00 M $HClO_4$

Temp, °C	$10^4[IrBr_6^{3-}]_0$, M	$10^4 k$,^{a} s^{-1}
10.0	5.71	0.38^b
10.0	5.71	0.37^c
15.1	8.61	1.22^b
15.1	8.72	1.28^c
25.0	3.73	6.30^b
25.0	3.73	6.13^c
25.0	15.2	6.18^d
29.9	8.26	10.1^b
29.9	8.91	11.7^c
34.8	7.64	16.6^b
34.8	7.55	19.3^c

^{a} First-order rate constant for reaction 2 from eq 1. ^{b} Continuous monitoring at 436 nm. ^{c} Continuous monitoring at 375 nm. ^{d} Sampling and oxidation procedure at 732 nm (cf. Experimental Section).

Table III. Kinetics of Decomposition of Intermediate Produced in the $IrBr_6^{2-}$–Cr^{2+} Reaction^a

$10^4[IrBr_6^{2-}]_0$, M	$10^4[Cr^{2+}]_0$, M	$[H^+]$, M	Temp, °C	k,^{b} s^{-1}
0.798	0.571	0.57	15.1	0.242 ± 0.014
0.726	0.601	1.00	15.1	0.256 ± 0.041
0.333	0.304	1.00	15.1	0.227 ± 0.016
8.46	7.43	0.10	25.0	$0.662 \pm 0.008^{c,d}$
7.85	8.30	0.10	25.0	$0.664 \pm 0.015^{c,f}$
4.07	4.00	0.76	25.0	$0.632 \pm 0.002^{e,g}$
9.27	8.47	1.00	25.0	0.672 ± 0.007^c
8.12	8.30	1.00	25.0	$0.631 \pm 0.009^{c,h}$
0.962	0.502	0.57	35.3	2.01 ± 0.17
0.286	0.190	0.75	35.3	1.51 ± 0.11
0.608	0.476	1.0	35.0	1.95 ± 0.34
0.832	0.457	1.0	35.4	1.86 ± 0.22

^{a} Measurements at 1.00 M ionic strength followed at 280 nm. ^{b} Each entry is the average of two–five replicate experiments. ^{c} Measured at 360 nm. ^{d} Measured at 370 nm. ^{e} Measured at 380 nm. ^{f} Measured at 420 nm. ^{g} Measured at 460 nm. ^{h} Measured at 470 nm.

nm was followed as a function of time. An isosbestic point was observed at 341 nm for the first 90–95% of reaction, but at longer times, in particular at room temperature and above, scans did not go through the isosbestic point (perhaps because of additional loss of bromide ion from the aquopentabromoiridate(III) product). Therefore, rate constants for reaction 1 were obtained by nonlinear least-squares fitting of absorbance vs. time data to eq 1, using A_∞ and k_{obsd} as adjustable parameters. In all cases the adjusted value of A_∞ was within 2% of measured values at 5 half-lives. In the second procedure, a solution containing the desired amounts of $IrBr_6^{3-}$, $HClO_4$, and $NaClO_4$ was placed in a constant-temperature bath and 1-mL samples, withdrawn at appropriate time intervals, were diluted to 50 mL with 2.5 M $HClO_4$ containing 0.01 M NaBr. Bromine vapor was allowed to dissolve in the solution whereby $IrBr_6^{3-}$ and $IrBr_5OH_2^{2-}$ were quantitatively oxidized to $IrBr_6^{2-}$ and $IrBr_5OH_2^-$, respectively. The absorbances of the resulting solutions were measured at 735 nm and the rate constants were obtained as before.

Stoichiometric Measurements. The products of the $IrBr_6^{2-}$–Cr^{2+} reaction are $IrBr_6^{3-}$, $IrBr_5OH_2^{2-}$, $CrBr^{2+}$, and Cr^{3+}. The yields of the iridium and chromium complexes were measured spectrophotometrically and by an ion-exchange procedure, respectively. The desired volume of a Cr^{2+} solution in 1.0 M $HClO_4$ was added *to* the solution of $IrBr_6^{2-}$ containing the desired amount of $HClO_4$.[5] The decomposition of the binuclear intermediate was allowed to proceed for ca. 10 half-lives. The resulting solution was diluted to reduce the acid concentration to less than 0.05 M and then was added to an ion-exchange column of Dowex 50-X8 (100–200 mesh) kept at 5 °C. The iridium products passed through the resin whereas the chromium(III) products, $CrBr^{2+}$ and Cr^{3+}, were retained. Elution of the $CrBr^{2+}$ and Cr^{3+} was accomplished by 1 and 4 M perchloric acid, respectively, and the chromium content of the two fractions was estimated spectrophotometrically as CrO_4^{2-} after oxidation with alkaline hydrogen peroxide. When the iridium products were determined, an aliquot of the product solution was treated with bromine vapor, whereby $IrBr_6^{3-}$ and $IrBr_5OH_2^{2-}$ are oxidized quantitatively to the corresponding iridium(IV) complexes, and the mixture was analyzed spectrophotometrically at 700 nm where the molar absorbances of $IrBr_6^{2-}$ and $IrBr_5OH_2^-$ are 2620 and 1660 M^{-1} cm^{-1}, respectively.

For the reaction between $IrBr_6^{2-}$ and $Co(CN)_5^{3-}$, only the iridium products were determined. Since the reaction must be carried out in alkaline or neutral solution and the iridium(III) products undergo decomposition reactions under these conditions,[6] the following procedure was adopted. A solution of freshly prepared $Co(CN)_5^{3-}$ in basic solution was added to a solution of $IrBr_6^{2-}$ containing a sufficient amount of perchloric acid to neutralize the added alkali (! HCN). The decomposition of the intermediate was allowed to proceed for ~30 s at 0 °C or ~5 s at 25 °C, and then chilled 4 M perchloric acid was added to bring the hydrogen ion concentration to ~1 M. The iridium(III) products were oxidized to the corresponding iridium(IV) complexes, and the absorbance of the resulting solution was measured at 700 nm. The assumption that the only iridium products are $IrBr_6^{2-}$ and $IrBr_5OH_2^-$ was confirmed by measuring the absorbance at 655 nm, an isosbestic point with molar absorbance 1868 M^{-1} cm^{-1}.

Results

The absorption spectra of Ir(IV) and Ir(III) complexes measured in the present work are tabulated in Table I. The spectrum of purple $IrBr_6^{2-}$ was measured in 0.10–1.00 M

$HClO_4$ and was found to be stable for several days. The reduction of $IrBr_6^{2-}$ in acid medium with ascorbic acid, followed by immediate reoxidation with bromine vapor, was found to be reversible. The spectrum of blue $IrBr_5OH_2^-$ was obtained by allowing a solution of $IrBr_6^{3-}$ (obtained by ascorbic acid reduction of $IrBr_6^{2-}$) to aquate at 10 °C and then oxidizing the resulting $IrBr_5OH_2^{2-}$ with bromine.[7]

The Aquation of $IrBr_6^{3-}$. Values of the first-order rate constant for reaction 1 are collected in Table II. There is good agreement between the values obtained by continuous monitoring of the absorbance change at 436 or 375 nm. A single measurement using a sampling of the reaction mixture followed by oxidation with bromine is in excellent agreement with the values obtained by the first method. Application of Eyring's equation to the data in Table II yields $\Delta H^\ddagger = 26.3 \pm 1.1$ kcal/mol and $\Delta S^\ddagger = 14.7 \pm 3.6$ eu.

The $IrBr_6^{2-}$–Cr^{2+} Reaction. This reaction proceeds in two discernible stages. The first is the very fast disappearance of the $IrBr_6^{2-}$ which results, at least in part, in the formation of an intermediate which we formulate as the binuclear successor complex $Br_5Ir^{III}BrCr^{III}(OH_2)_5$. The second stage corresponds to the disappearance of the intermediate and results in the formation of mononuclear iridium(III) and chromium(III) products. The first stage, detected by the disappearance of the absorbance at 584 nm of $IrBr_6^{2-}$, is too fast to measure by stopped-flow techniques ($k > 10^6$ M^{-1} s^{-1}). The results of the kinetic studies of the second stage are summarized in Table
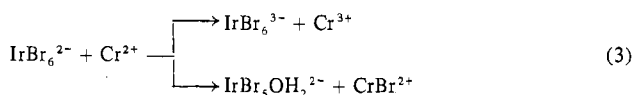
Table IV. Stoichiometry of the $IrBr_6^{2-}-Cr^{2+}$ Reaction[a]

$10^3[Ir-Br_6^{2-}]_0$, M	$10^3[Cr^{2+}]_0$, M	Temp, °C	% $IrBr_5OH_2^{-}$ [b]	% $CrBr^{2+}$ [c]
1.09	1.00	0.0	32	
1.32	1.25	5.0	27	
1.84	1.79	10.0	35	
1.43	1.35	15.0	35	
1.73	1.37	20.0	40	
2.73	2.57	0.0		27^d
2.67	2.6^e	15.0		34^f
0.17	0.17^e	25.0		41, 42
3.86	3.8^e	25.0		40
0.83	0.83	25.0		36
0.85	0.74	25.0		36^g
2.28	2.2^e	35.0		47^h

[a] Unless specified otherwise $[HClO_4] = 1.0$ M. [b] Measured spectrophotometrically at 700 nm following oxidation by Br_2. Based on amount of $IrBr_6^{2-}$ reacted. [c] Measured following ion exchange separation. Based on amount of $IrBr_6^{2-}$ reacted. [d] $[HClO_4] = 0.33$ M. [e] Estimated by dropwise addition of Cr^{2+} solution to a visual end point. [f] $[HClO_4] = 0.70$ M. [g] $[HClO_4] = 0.10$ M. [h] $[HClO_4] = 0.67$ M.

III. The disappearance of the intermediate proceeds by first-order kinetics, the first-order rate constant being independent of initial Cr^{2+} and $IrBr_6^{2+}$ concentrations, of acidity, and of wavelength of observation. The average value of the rate constant at 25 °C is $(6.52 \pm 0.17) \times 10^{-1}$ s^{-1}, and the corresponding activation parameters are $\Delta H^\ddagger = 17.0 \pm 0.5$ kcal/mol and $\Delta S^\ddagger = 2.4 \pm 1.8$ eu.

The final mononuclear chromium(III) and iridium(III) products were estimated quantitatively by the methods described in the Experimental Section, and the results are summarized in Table IV. The overall stoichiometry of the reaction is represented by eq 3, and the results of chromium

$$IrBr_6^{2-} + Cr^{2+} \begin{cases} \longrightarrow IrBr_6^{3-} + Cr^{3+} \\ \longrightarrow IrBr_5OH_2^{2-} + CrBr^{2+} \end{cases} \quad (3)$$

and iridium analyses are internally consistent to about 5%.

The absorption spectrum of the intermediate was obtained by measuring the initial absorbance of the solution and subtracting the contribution of the excess reactant (generally $IrBr_6^{2-}$). The intermediate displays a broad maximum centered around 440 nm. The molar absorptivity of the intermediate can be calculated under two different assumptions. If the intermediate is formed in 100% yield, the molar absorptivity is 4.5×10^2 M^{-1} cm^{-1}. If the intermediate is formed in 40% yield (the observed yields of $IrBr_5OH_2^{2-}$ and $CrBr^{2+}$), the molar absorptivity is 8.5×10^2.

The $IrBr_6^{2-}-Co(CN)_5^{3-}$ Reaction. This reaction also proceeds in two stages. The first stage is the very fast disappearance of $IrBr_6^{2-}$ by reaction with $Co(CN)_5^{3-}$ ($k > 10^6$ M^{-1} s^{-1}) which produces, at least in part, an intermediate formulated as $Br_5Ir^{III}BrCo^{III}(CN)_5^{5-}$. The second stage corresponds to the disappearance of the intermediate to form mononuclear iridium(III) and cobalt(III) products, and the pertinent kinetic studies are summarized in Table V. It will be seen that the decomposition of the intermediate is a first-order process independent of initial $IrBr_6^{2-}$ and $Co(CN)_5^{3-}$ concentrations, of excess cyanide concentration, and of wavelength. The average value of the rate constant at 25 °C is 5.63 ± 0.18 s^{-1}, and the corresponding activation parameters are $\Delta H^\ddagger = 14.9 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -5.1 \pm 1.2$ eu.

The final iridium(III) mononuclear products were estimated spectrophotometrically as described in the Experimental Section. Ten measurements were carried out at 0 °C with $[IrBr_6^{2-}]_0 = [Co(CN)_5^{3-}]_0$ in the concentration range $(0.96-8.55) \times 10^{-4}$ M. The yield of $IrBr_5OH_2^{2-}$ was $41 \pm 5\%$.

Table V. Kinetics of Decomposition of Intermediate Produced in the $IrBr_6^{2-}-Co(CN)_5^{3-}$ Reaction[a]

$10^4[Ir-Br_6^{2-}]_0$, M	$10^4[Co-(CN)_5^{3-}]_0$, M	$10^3[CN^-]$, M	Temp, °C	k,[b] s^{-1}
0.130	0.400	0.20	15.0	2.24 ± 0.07^c
0.734	1.04	1.19	15.0	2.11 ± 0.13
0.973	3.00	3.02	15.0	2.49 ± 0.12
1.39	2.80	5.60	15.0	2.29 ± 0.14
0.734	1.04	1.19	25.0	5.63 ± 0.11
0.944	20.0	20.5	25.0	5.51 ± 0.17
0.973	3.00	3.02	25.0	5.62 ± 0.11
0.993	20.0	20.0	25.0	5.87 ± 0.19
1.39	2.80	5.60	25.0	5.91 ± 0.11
1.52	3.00	30.0	25.0	5.42 ± 0.03
3.18	4.00	4.60	25.0	5.44 ± 0.22^d
0.660	1.16	1.21	35.0	13.0 ± 0.9
0.765	2.00	1.99	35.0	13.7 ± 0.3
0.973	3.00	3.02	35.0	11.7 ± 0.8
0.993	20.0	20.0	35.0	14.5 ± 0.9
1.39	2.80	5.60	35.0	14.6 ± 0.7
1.52	3.00	30.0	35.0	12.4 ± 0.7

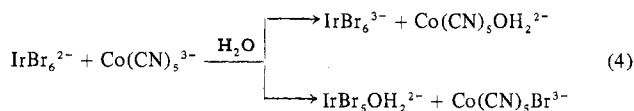[a] Measurements at ionic strength 0.10 M and $[OH^-] = 1.0 \times 10^{-2}$ M followed at 330 nm. [b] Each entry is the average of five–seven replicate experiments. [c] Followed at 265 nm. [d] Average of 23 experiments measured at 10-nm intervals from 500 to 330 nm.

Table VI. Yield of Intermediate in the $IrBr_6^{2-}-Co(CN)_5^{3-}$ Reaction[a]

$10^4[Ir-Br_6^{2-}]_0$, M	$10^4[Co-(CN)_5^{3-}]_0$, M	$10^3[CN^-]$, M	Temp, °C	$10^{-2}A/[Ir-Br_6^{2-}]_0$,[b] M^{-1}
0.734	1.04	1.20	15.0	8.8 ± 0.4
0.973	3.00	3.00	15.0	9.6 ± 0.4
1.39	2.80	5.60	15.0	8.0 ± 0.4
0.734	1.04	1.20	25.0	9.8 ± 0.2
0.973	3.00	3.00	25.0	9.8 ± 0.2
1.39	2.80	5.60	25.0	7.4 ± 0.2
1.52	3.00	30.0	25.0	8.6 ± 0.2
0.660	1.16	1.20	35.0	9.0 ± 0.3
0.765	2.00	2.00	35.0	8.8 ± 0.2
0.973	3.00	3.00	35.0	11 ± 0.2
1.39	2.80	5.60	35.0	7.1 ± 0.4
1.52	3.00	30.0	35.0	9.0 ± 0.2

[a] Measurements at ionic strength 0.10 M and $[OH^-] = 1.0 \times 10^{-2}$ M. [b] A is the initial absorbance of the solution corrected for the absorbance of the excess $Co(CN)_5^{3-}$; wavelength 330 nm, path length 0.20 cm. Each entry is the average of four or five replicate measurements.

Four experiments at 25 °C gave a $IrBr_5OH_2^{2-}$ yield of $42 \pm 3\%$. Therefore, the overall stoichiometry of the reaction is represented by eq 4.

$$IrBr_6^{2-} + Co(CN)_5^{3-} \xrightarrow{H_2O} \begin{cases} \longrightarrow IrBr_6^{3-} + Co(CN)_5OH_2^{2-} \\ \longrightarrow IrBr_5OH_2^{2-} + Co(CN)_5Br^{3-} \end{cases} \quad (4)$$
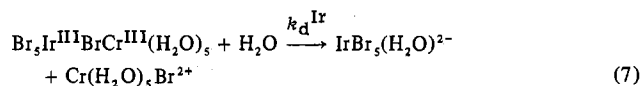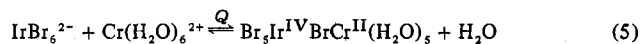
Although it is not possible to obtain an absolute value of the yield of the intermediate, the initial absorbance of the solution obtained by mixing $IrBr_6^{2-}$ and $Co(CN)_5^{3-}$ provides a relative measure of the amount of intermediate produced under various conditions. The results are summarized in Table VI, and it will be seen that the yield of the intermediate is independent of initial $IrBr_6^{2-}$ and $Co(CN)_5^{3-}$ concentrations, of excess CN^- concentration, and of temperature.

The intermediate displays absorption maxima at 480 and 410 nm with molar absorptivities, calculated assuming that the intermediate is produced in 100% yield, equal to 1.3×10^3
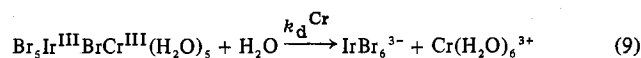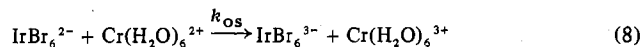
and 1.5×10^3 M^{-1} cm^{-1}, respectively.

Discussion

The substantial transfer of bromide ion from oxidant to reductant in the reactions of $IrBr_6^{2-}$ with Cr^{2+} and with $Co(CN)_5^{3-}$ shows that these reactions proceed, at least in part, by an inner-sphere mechanism. It is generally accepted[8] that an inner-sphere redox reaction proceeds in three stages, namely, formation of a precursor binuclear complex, intramolecular electron transfer to form a successor binuclear complex, and dissociation of the successor complex. For the portion of the $IrBr_6^{2-}$–Cr^{2+} reaction that results in bromide ion transfer the stages are shown in eq 5–7. Assuming that

$$IrBr_6{}^{2-} + Cr(H_2O)_6{}^{2+} \overset{Q}{\rightleftharpoons} Br_5Ir^{IV}BrCr^{II}(H_2O)_5 + H_2O \tag{5}$$

$$Br_5Ir^{IV}BrCr^{II}(H_2O)_5 \xrightarrow{k_{et}} Br_5Ir^{III}BrCr^{III}(H_2O)_5 \tag{6}$$

$$Br_5Ir^{III}BrCr^{III}(H_2O)_5 + H_2O \xrightarrow{k_d{}^{Ir}} IrBr_5(H_2O)^{2-} + Cr(H_2O)_5Br^{2+} \tag{7}$$

the strong charge-transfer absorption of $IrBr_6^{2-}$ would be retained in the precursor complex, the results of the kinetic measurements show that reactions 5 and 6 are too rapid to be measured with $Qk_{et} > 10^6$ M^{-1} s^{-1}, and it is suggested that the intermediate detected is the successor binuclear complex which decomposes at a measurable rate. The mechanism depicted in eq 5–7 for the portion of the reaction that results in bromide ion transfer is identical with that proposed previously for the analogous $IrCl_6^{2-}$–Cr^{2+} reaction.[3]

Two different pathways can be invoked to account for the formation of $IrBr_6^{3-}$ and $Cr(H_2O)_6^{3+}$, e.g., the portion of the reaction that proceeds without bromide ion transfer. These are an outer-sphere pathway (eq 8) and the dissociation of the

$$IrBr_6{}^{2-} + Cr(H_2O)_6{}^{2+} \xrightarrow{k_{os}} IrBr_6{}^{3-} + Cr(H_2O)_6{}^{3+} \tag{8}$$

$$Br_5Ir^{III}BrCr^{III}(H_2O)_5 + H_2O \xrightarrow{k_d{}^{Cr}} IrBr_6{}^{3-} + Cr(H_2O)_6{}^{3+} \tag{9}$$

successor complex via Cr–Br bond breaking (eq 9). These alternatives were previously[3] considered for the analogous $IrCl_6^{2-}$–Cr^{2+} reaction, and it was concluded on the basis of convincing, albeit indirect, arguments that the outer-sphere mechanism was operative. We have been able to obtain direct, experimental evidence bearing on this question. On the basis of the data reported previously,[3] the $IrCl_6^{2-}$–Cr^{2+} reaction at 0 °C proceeds 76% via the outer-sphere pathway and 24% via the inner-sphere pathway, and the binuclear successor complex has a half-life of ~8 min. With this relatively long half-life, it is possible to effect a separation on a cation-exchange resin of the $Cr(H_2O)_6^{3+}$ produced in the outer-sphere pathway from the binuclear successor $Cl_5IrClCr(H_2O)_5$ produced in the inner-sphere pathway. The experiment was carried out by adding 1.20 mL of 0.0406 M Cr^{2+} to 4.78×10^{-5} mol of $IrCl_6^{2-}$ in 30 mL of 0.10 M $HClO_4$ at 0 °C followed immediately by 200 mL of ice-cold water. The resulting solution was passed rapidly (82 s) through a column of Dowex 50-X8, 100–200 mesh, H^+ form. The hexaaquochromium(III) ion retained in the column was eluted with 4.0 M $HClO_4$ and analyzed. It was found that 71% of the chromium that reacted was retained as $Cr(H_2O)_6^{3+}$ in the cation resin. The binuclear complex that went through the resin was allowed to dissociate, and the $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5Cl^{2+}$ produced were analyzed. It was found that the dissociation of the binuclear complex produced 61% $Cr(H_2O)_5Cl^{2+}$ and 39% $Cr(H_2O)_6^{3+}$. These results show conclusively that the Cr^{2+}–$IrCl_6^{2-}$ reaction proceeds via parallel inner-sphere and outer-sphere reactions, in agreement with the previous conclusion.[3] But in addition, the results demonstrate that the dissociation of the binuclear

complex proceeds via two pathways involving Ir–Cl and Cr–Cl bond rupture, respectively. Because of the greater rate of dissociation of $Br_5IrBrCr(H_2O)_5$ (~10-s half-life at 0 °C), the direct test to ascertain the source or sources of $Cr(H_2O)_6^{3+}$ and $IrBr_6^{3-}$ cannot be performed. However, in view of the similarity between the chloride and bromide systems, it seems reasonable to conclude that the mechanism represented by eq 5–9 is operative; e.g., the redox reaction proceeds via parallel inner-sphere and outer-sphere pathways, and dissociation of the successor complex occurs via parallel Ir–Br and Cr–Br bond-rupture reactions.
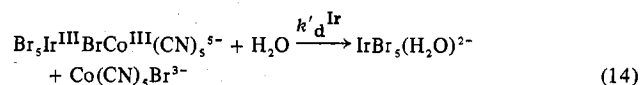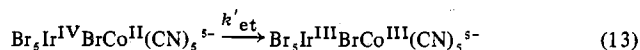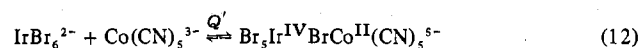
Although Cr^{2+} has an overwhelming tendency to react via an inner-sphere mechanism, substitution into the coordination sphere of chromium(II) may be bypassed for very reactive oxidants, and an outer-sphere mechanism becomes operative.[10] Only the lower limit of 10^6 M^{-1} s^{-1} can be placed on the rate constants for the outer-sphere reactions of Cr^{2+} with $IrCl_6^{2-}$ or $IrBr_6^{2-}$, but it is likely that these rate constants are appreciably higher. A calculation of k_{12}, the rate constant for the outer-sphere reaction between $IrCl_6^{2-}$ and Cr^{2+}, can be made using Marcus' cross relation[11]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{10}$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \tag{11}$$

The value of $K_{12} = 1.73 \times 10^{24}$, the equilibrium constant for the $IrCl_6^{2-}$–Cr^{2+} reaction, is calculated from the reduction potentials of the $IrCl_6^{2-/3-}$ (1.02 V) and $Cr^{3+/2+}$ (−0.41 V) couples.[12] k_{11}, the rate constant for the $IrCl_6^{2-}$–$IrCl_6^{3-}$ exchange reaction, is 2.3×10^5 M^{-1} s^{-1}.[13] Unfortunately, k_{22}, the rate constant for the Cr^{2+}–Cr^{3+} exchange reaction, is unknown. However, a value of k_{22} can be estimated from the measured rate constants for the outer-sphere reactions of Cr^{2+} with $Ru(NH_3)_5py^{3+}$ [14] and $Co(phen)_3^{3+}$ [15] through the application of eq 10 and 11. The values of k_{22} obtained in this manner are 5.5×10^{-10} and 4.7×10^{-10} M^{-1} s^{-1}, respectively, and the excellent agreement between the two values gives some confidence as to the reliability of the method of estimation. Using the average value $k_{22} = 5.1 \times 10^{-10}$ and the values of k_{11} and K_{12} given above and applying the necessary electrostatic correction to eq 10,[16] we obtain $k_{12} = 5.5 \times 10^8$ M^{-1} s^{-1}. A similar calculation[17] for reaction 8 yields a value of $k_{os} = 3.8 \times 10^9$ M^{-1} s^{-1}. These rates are sufficiently fast to be competitive with substitution into the coordination sphere of chromium(II), and therefore it is reasonable to find that parallel inner-sphere and outer-sphere mechanisms obtain in these systems.

The portion of the $IrBr_6^{2-}$–$Co(CN)_5^{3-}$ reaction that results in bromide ion transfer proceeds, most likely, through the three stages given by eq 12–14. The first two stages are too rapid
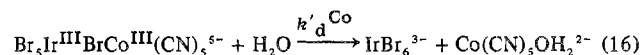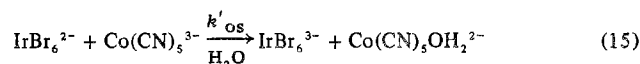
$$IrBr_6{}^{2-} + Co(CN)_5{}^{3-} \overset{Q'}{\rightleftharpoons} Br_5Ir^{IV}BrCo^{II}(CN)_5{}^{5-} \tag{12}$$

$$Br_5Ir^{IV}BrCo^{II}(CN)_5{}^{5-} \xrightarrow{k'_{et}} Br_5Ir^{III}BrCo^{III}(CN)_5{}^{5-} \tag{13}$$

$$Br_5Ir^{III}BrCo^{III}(CN)_5{}^{5-} + H_2O \xrightarrow{k'_d{}^{Ir}} IrBr_5(H_2O)^{2-} + Co(CN)_5Br^{3-} \tag{14}$$

to be measured, $Q'k'_{et} > 10^6$ M^{-1} s^{-1}, and the successor binuclear complex, the intermediate detected in the reaction, decomposes at a measurable rate. The entirely analogous intermediate $Cl_5IrClCo(CN)_5^{5-}$ was previously identified in the $IrCl_6^{2-}$–$Co(CN)_5^{3-}$ reaction.[4]

Two alternative pathways can be considered to account for the portion of the $IrBr_6^{2-}$–$Co(CN)_5^{3-}$ that proceeds without bromide ion transfer: a parallel outer-sphere reaction (eq 15) and the dissociation of the intermediate via Co–Br bond breaking (eq 16). Unfortunately, the binuclear intermediate

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Table VII. Rate Constants and Activation Parameters for Dissociation of Bromide and Chloride Complexes

Complex	k, s⁻¹ (25 °C)	$\Delta H^{\ddagger}$, kcal/ mol	$\Delta S^{\ddagger}$, eu	% Ir–X bond rupture Obsd	% Ir–X bond rupture Predict-ed[a]	Ref
Br₅IrBrCr(H₂O)₅	6.5×10^{-1}	17.0	−2.4	>40	65	b
Br₅IrBrCo(CN)₅⁵⁻	5.6	14.9	−5.1	>41	83	b
Cl₅IrClCr(H₂O)₅	4.2×10^{-2}	21.8	8.4	40[c]	85	d
Cl₅IrClCo(CN)₅⁵⁻	4.0	15.4	−4.2	<2	2	e
IrBr₆³⁻	6.2×10^{-4}	26.3	14.7			b
Cr(H₂O)₅Br²⁺	5.7×10^{-5}	23.8	−3.5			f
Co(CN)₅Br³⁻	2.2×10^{-5}	24.1	1.1			g
IrCl₆³⁻	9.4×10^{-6}	29.4	19			h
Cr(H₂O)₅Cl²⁺	2.8×10^{-7}	24.4	−7			i
Co(CN)₅Cl³⁻	6.4×10^{-5}	23.2	0			g

[a] This is $100r/6(r + 1)$ where r is the ratio of the rate constant for aquation of IrX_6^{3-} (X = Br, Cl) to the rate constant for aquation of $Cr(H_2O)_5X^{2+}$ or $Co(CN)_5X^{3-}$ (X = Br, Cl). [b] This work. [c] At 0 °C. [d] Reference 3. [e] Reference 4. [f] F. A. Guthrie and E. L. King, *Inorg. Chem.*, 3, 916 (1964). [g] R. G. Grassi, A. Haim, and W. K. Wilmarth, *ibid.*, 6, 237 (1967). [h] Reference 6. [i] T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

$$IrBr_6^{2-} + Co(CN)_5^{3-} \xrightarrow[H_2O]{k'_{os}} IrBr_6^{3-} + Co(CN)_5OH_2^{2-} \quad (15)$$

$$Br_5Ir^{III}BrCo^{III}(CN)_5^{5-} + H_2O \xrightarrow{k'_d{}^{Co}} IrBr_6^{3-} + Co(CN)_5OH_2^{2-} \quad (16)$$

is short-lived ($t_{1/2} \approx 1$ s at 0 °C and ~15 s for the corresponding chloride complex[4]), and therefore stoichiometric measurements of product distribution before the intermediate decomposes are precluded. However, the indirect arguments used previously[4] to rule out an outer-sphere contribution for the $Co(CN)_5^{3-}$–$IrCl_6^{2-}$ reaction are still applicable to the present system. Moreover, the temperature independence of the ratio $[IrBr_5(H_2O)^{2-}]/[IrBr_6^{3-}]$ produced in the reaction suggests competitive bond-breaking processes of the successor complex (eq 14 and 16) with little or no difference in enthalpies of activation, rather than parallel inner- and outer-sphere pathways (eq 12, 13, and 15) for which substantial differences in enthalpies of activation have been recorded previously.[3,18] Admittedly, the arguments are indirect, but they suggest that the mechanism of the $IrBr_6^{2-}$–$Co(CN)_5^{3-}$ reaction is best described on the basis of eq 12–14 and 16, with little or no participation of eq 15.

If the mechanistic conclusions presented above are accepted, then the inner-sphere portions of the Cr^{2+}–$IrBr_6^{2-}$ and $Co(CN)_5^{3-}$–$IrBr_6^{2-}$ reactions proceed only with partial bridging ligand transfer from oxidant to reductant. It is well recognized by now[8,9] that bridging ligand transfer is not an essential feature of the inner-sphere mechanism. Whether or not ligand transfer takes place depends on the position of bond rupture when the binuclear successor complex dissociates to form mononuclear products. The dissociation of the binuclear complexes may be viewed as metal-catalyzed aquations of the parent complexes, and the pertinent information is summarized in Table VII. It will be seen that the rates of dissociation of the binuclear complexes are 10^4–10^5 faster than the rates for the corresponding parent mononuclear complexes, the increase in rate being associated with a decrease in the enthalpies of activation by 8–10 kcal and the complementary decrease in the entropy of activation. Similar trends have been observed before in typical metal ion catalyzed aquations.[19] It is noteworthy that the position of bond rupture in the binuclear complexes correlates reasonably well with what is expected on the basis of the rates of dissociation of the corresponding mononuclear complexes. Thus, $Br_5IrBrCr(H_2O)_5$ dissociates with at least 40% Ir–Br bond rupture; the ratio of the rate constants for aquations of $IrBr_6^{3-}$ and $Cr(H_2O)_5Br^{2+}$ is 10.9, but the ratio has to be corrected for the statistical factor of 6. Therefore, the amount of Ir–Br bond breaking predicted on the basis of the corrected ratio is 65%. The observed and predicted percents of Ir–halogen bond ruptures are presented in Table VII, and, considering the simplicity of the approach, the agreement is taken to be satisfactory.

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(1) This work was supported by Grants GP-37057 and CHE76-10449 from the National Science Foundation.
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(5) In all cases, $[Cr^{2+}]_0 \leq [IrBr_6^{2-}]_0$. High and nonreproducible yields of $CrBr^{2+}$ were obtained when Cr^{2+} was in excess, perhaps because the excess Cr^{2+} reduces the Ir(III) products.
(6) The difficulties encountered are entirely analogous to those described for the corresponding chloro complexes: I. A. Poulsen and C. S. Garner, *J. Am. Chem. Soc.*, **84**, 2032 (1962).
(7) Our values of λ_{max} for $IrBr_6^{2-}$ and $IrBr_6^{3-}$ are in good agreement with those reported by C. K. Jorgensen, *Acta Chem. Scand.*, **10**, 500, 517 (1956), but our values of A_M differ by ca. 30% in the case of $IrBr_6^{3-}$ and by about 20% for $IrBr_6^{2-}$. Our value of A_M at 584 nm for $IrBr_6^{2-}$ agrees well with the value (3.80×10^3) reported by P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964).
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(17) In order to do the calculation, the rate constant for the $IrBr_6^{2-}$–$IrBr_6^{3-}$ exchange reaction must be available. This was estimated to be 1.6×10^8 M⁻¹ s⁻¹ from the data in ref 13.
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