energetics especially since the alternative REAO mechanism seems inoperative (see above). The reactions therefore cover a mechanistic spectrum from S_N1cB through S_N1ip and, possibly, to S_N2,[30] this range[31] of mechanisms being made evident by the variation in the stereochemical changes, the 90 kJ mol^{-1} range of $\Delta H_2^‡$ and the 75 kJ mol^{-1} range of $\Delta H_2^‡-\Delta H_1^‡$.

Acknowledgment. We thank Mr. J. J. Stamers and Mrs. I. Walker for performing some of the runs on the *trans*-Rh(en)$_2$ICl$^+$/Br$^-$ system. We are grateful to Erindale College and the National Research Council of Canada for financial support.

Registry No. *trans*-Rh(en)$_2$ICl$^+$, 55721-97-6; *trans*-Rh(en)$_2$I$_2$$^+$, 24444-41-5; OH$^-$, 14280-30-9; Cl$^-$, 16887-00-6; Br$^-$, 24959-67-9.

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(29) Pavelich, M. J. *Inorg. Chem.* **1975**, *14*, 982.

(30) The ip in S_N2ip is redundant since any S_N2 reaction must inevitably occur via an encounter complex of some kind.

(31) The possibility of an S_N1cB–S_N1ip mechanistic spectrum was, of course, suggested some time ago by Chan and Lau.[32] This is the first time that the possibility has been so strongly indicated by detailed and systematic variations of energetic and stereochemical behavior for a series of closely related reactions.

(32) Chan, S. C.; Lau, O. W. *Aust. J. Chem.* **1969**, *22*, 1851.

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Chromium(III) Products from the Reduction of 1,4-Benzoquinone by Chromous Ion. Synthesis of the μ-Oxo-bis(pentaaquochromium(III)) Ion

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The chromium(III) products resulting from the reduction of 1,4-benzoquinone (BQ) by chromous ion in weakly and strongly acidic solutions have been isolated through cation-exchange chromatography on SP-Sephadex C-25 resin. Five chromium-containing products were obtained from the anaerobic addition of 1.25 mL of 0.460 M Cr(ClO$_4$)$_2$–0.117 M HClO$_4$ to 0.60 mmol of benzoquinone dissolved in 50 mL of water: Cr(H$_2$O)$_6$$^{3+}$ (42%); a 2:1 ratio chromium(III)–hydroquinone complex (35%), proposed to be [(H$_2$O)$_4$Cr(OH)(HQ)Cr(H$_2$O)$_4$]$^{4+}$; an oxo-bridged binuclear complex (4%), [(H$_2$O)$_5$CrOCr(H$_2$O)$_5$]$^{4+}$; a 3:1 Cr^{III}–H$_2$Q complex (15%); and a small amount of a golden yellow product which could not be eluted from SP-C-25 resin. A much larger initial yield of [(H$_2$O)$_5$CrOCr(H$_2$O)$_5$]$^{4+}$ was obtained from the addition of Cr^{2+}(aq) to benzoquinone dissolved in 0.1 M HClO$_4$, but this product is unstable in acidic solution, yielding Cr(H$_2$O)$_6$$^{3+}$ as the predominant (75%) chromium species eluted from the cation-exchange column. Much less of the 2:1 Cr^{III}–H$_2$Q complex was formed from the Cr^{II}–BQ reaction in 0.1 M HClO$_4$ (3%), and a second 3:1 Cr^{III}–H$_2$Q complex (19%) was produced under these conditions. The UV–visible absorption spectra of the chromium(III) products are reported, and the implications of the product distribution studies for the mechanism of electron transfer from chromium(II) to benzoquinone are discussed.

Introduction

Kinetic studies of the reduction of *Rhus vernicifera* laccase type 1 copper by substituted hydroquinones[1] prompted our interest in the effect of coordination on the electron-transfer reactivity of these organic substrates. We planned, therefore, to examine the oxidation mechanism of chromium(III)-complexed hydroquinone (H$_2$Q) in the (hydroquinonato)pentaaquochromium(III) ion and related species. Reduction of 1,4-benzoquinone (BQ) by the (pentacyano)cobaltate(II) ion yields a binuclear cobalt(III) complex, [(NC)$_5$CoOC$_6$H$_4$OCo(CN)$_5$]$^{6-}$, containing a bridging group isoelectronic with the dianion of hydroquinone.[2] The mononuclear [(NC)$_5$CoOC$_6$H$_4$OH]$^{3-}$ ion was obtained through partial hydrolysis of the binuclear complex.[2] By analogy with these results for Co(CN)$_5$$^{2-}$ as the reductant, we expected to obtain [(H$_2$O)$_5$CrOC$_6$H$_4$OCr(H$_2$O)$_5$]$^{4+}$ and [(H$_2$O)$_5$CrOC$_6$H$_4$OH]$^{2+}$ as the predominant chromium(III) products in the reaction of 1,4-benzoquinone with chromous ion in aqueous solution. This expectation was in fact not realized, but a number of other interesting products, including the μ-oxo-bis(pentaaquochromium(III)) ion, were obtained through the reduction of benzoquinone by Cr^{2+}(aq). In this paper we report product distribution studies for the reaction of Cr^{2+}(aq) with benzoquinone in both weakly and strongly acidic solutions. The implications of these distribution studies for the mechanism of electron transfer from Cr(II) to BQ are discussed.

Experimental Section

Materials. Reagent grade chemicals were used throughout. Reactions were carried out in solutions prepared with triply distilled water, and eluant solutions were prepared with doubly distilled water. Cr(ClO$_4$)$_3$·6H$_2$O, Ce(ClO$_4$)$_3$·6H$_2$O, LiClO$_4$, and 0.5 N Ce(ClO$_4$)$_4$ in 6 N HClO$_4$ were used as supplied by G. F. Smith. Practical grade 1,4-benzoquinone was purified through vacuum sublimation. SP-Sephadex C-25-120 resin was used in all cation-exchange experiments. Acidic solutions of the di-μ-hydroxo-bis(tetraaquochromium(III)) ion were obtained through the aerobic oxidation of chromous ion, as described by Ardon and Plane.[3]

Solutions in serum-capped bottles were made anaerobic by purging with chromous-scrubbed nitrogen for at least 40 min. Teflon needles were used in purging solutions, while stainless-steel needles and Hamilton gastight syringes were employed in transferring anaerobic solutions. A chromous perchlorate stock solution was prepared by reducing anaerobic 0.460 M Cr(ClO$_4$)$_3$ in 0.117 M HClO$_4$ over 4% zinc amalgam.

Analyses. Chromium(II) stock solutions were assayed by injecting aliquots into an excess of acidic Fe(III). The Fe(II) produced was then titrated with standard Cr$_2$O$_7$$^{2-}$ to a diphenylaminesulfonate end point. Hydroquinone (ϵ_{288} = 2.30 × 10^3 M^{-1} cm^{-1})[4] and benzoquinone (ϵ_{246} = 2.18 × 10^4 M^{-1} cm^{-1})[5] concentrations were determined spectrophotometrically in solutions containing no Cr. Correction was made for the absorption of benzoquinone at 288 nm[5] when [H$_2$Q]

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(1) Clemmer, J. D.; Gilliland, B. L.; Bartsch, R. A.; Holwerda, R. A. *Biochim. Biophys. Acta* **1979**, *568*, 307–20.

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(5) Baxendale, J. H.; Hardy, H. R.; Sutcliffe, L. H. *Trans. Faraday Soc.* **1951**, *47*, 963–73.

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was determined in solutions containing both H_2Q and BQ. Hydroquinone interference in the spectrophotometric assay of [BQ] at 246 nm was shown to be negligible.

Total chromium in the chromic perchlorate stock solution was assayed spectrophotometrically by the basic peroxide method ($\epsilon_{373}(CrO_4^{2-})$ = 4815 M^{-1} cm^{-1}).[6] SP-Sephadex C-25 resin was used to separate Cr from H_2Q in assays of chromium(III)–hydroquinone complexes. Acidic solutions of these complexes eluted from cation-exchange columns were allowed to fully aquate to $Cr(H_2O)_6^{3+}$ and H_2Q at room temperature (ca. 2–3 days). Aliquots were then diluted with distilled water and absorbed onto 8 × 1.5 cm SP-C-25 columns (Na^+ form). Hydroquinone was washed through the column with water and assayed spectrophotometrically, leaving all of the Cr absorbed on the resin. Chromium was then quantitatively removed from the resin by oxidation to CrO_4^{2-} with basic peroxide. After boiling to destroy excess H_2O_2 and filtration to remove the resin, $[CrO_4^{2-}]$ in these solutions was obtained by measuring the absorbance at 373 nm.

Stoichiometry of the Cr^{II}–BQ Reaction. The overall stoichiometry of the Cr^{II}–BQ reaction was determined by injecting aliquots of Cr^{2+}(aq) into excess benzoquinone, dissolved in distilled water or 0.1 M $HClO_4$. The hydroquinone produced was then determined as above following complete hydrolysis of the chromium(III)–hydroquinone products and separation of $Cr(H_2O)_6^{3+}$ from H_2Q and BQ on a SP-C-25 column. Results from four independent determinations showed that 0.62 ± 0.01 mol of H_2Q was produced/mol of Cr(II) consumed, in poor agreement with the value of 0.50 mol of H_2Q/mol of Cr(II) expected for the overall process in eq 1. It was shown,

$$2Cr^{II} + BQ \rightarrow 2Cr^{III} + H_2Q \tag{1}$$

however, that considerable reduction of BQ to H_2Q (typically 25–30%) occurred upon passage through SP-C-25 columns in the Na^+ form. Correction of the stoichiometry results for column-induced BQ reduction yielded a value of 0.48 ± 0.02 mol of H_2Q/mol of Cr(II), consistent with the expected stoichiometry. Results given below for the amount of hydroquinone appearing free in solution following the reaction of Cr^{2+}(aq) with excess benzoquinone have been similarly corrected for H_2Q resulting from column-induced reduction of BQ.

Instrumentation. UV-visible spectra were measured on a Cary 17 spectrophotometer. Chromatographic separations of Cr^{2+}(aq)–BQ product mixtures were carried out at 5 °C, in a Masterbilt cold case. Absorption spectra of the chromium-containing products were obtained at 5 °C immediately following their elution from SP-C-25 columns.

Results

I. Addition of Cr^{2+}(aq) to Benzoquinone in Aqueous Solution. A dark green solution results from the slow anaerobic addition of 1.25 mL of 0.460 M $Cr(ClO_4)_2$–0.117 M $HClO_4$ (0.575 mmol of Cr(II)) to an excess of 1,4-benzoquinone (0.60 mmol) dissolved in 50 mL of distilled water (0 °C). Five chromium-containing bands were observed upon absorption of the product mixture onto a 15 × 2.5 cm SP-C-25 cation-exchange column (Na^+ or Li^+ form) followed by elution with acidic $LiClO_4$ solutions. Excess benzoquinone and free hydroquinone were washed through the column with 0.1 M $LiClO_4$-0.1 M $HClO_4$; 51% of the total H_2Q produced was not retained on the column. A blue-violet cation was then eluted with 0.5 M $LiClO_4$–0.1 M $HClO_4$. This component exhibited a visible absorption spectrum identical with that of $Cr(H_2O)_6^{3+}$ (broad, weak maxima at 574 and 408 nm)[6,7] and accounted for 42% of the total Cr but only 1% of the H_2Q in the product mixture. In some runs, a faint pink band was eluted ahead of $Cr(H_2O)_6^{3+}$. This species, thought to be a chromium(III)–benzoquinone complex, accounted for a negligible fraction of the total Cr in the product mixture.

Following the well-separated blue-violet first band were closely spaced olive green (complex I, leading) and yellow-brown (complex II) components. Both of these cations were eluted with 1 M $LiClO_4$–0.1 M $HClO_4$, leaving a yellow-green band (complex III) halfway down the column and a pale golden yellow band at the top. The olive green cation contains Cr and hydroquinone in a 2 (1.95 ± 0.08):1 ratio. The absorption spectrum of complex I is characterized by a broad band with maximum at 603 nm, a poorly resolved shoulder near 440 nm, and a sharp, intense peak at 298 nm. Spectral data for complex I and other new Cr species identified in this study are summarized in Table I. Complex I accounted for 35% of the chromium in the product mixture, while only 4% of the total Cr appeared as complex II. No hydroquinone or benzoquinone was found in the yellow-brown fraction.

Table I. UV-Visible Spectral Data[a]

complex	compn, mol of Cr:mol of H_2Q	λ_{max}, nm	ϵ, M^{-1} cm^{-1} [b]
I[c]	2:1	603	6.9 × 10
		440 (sh)	1.9×10^2
		298	4.1×10^3, 8.2×10^3 [f]
II[d]	2:0	632	2.0×10^2
		587	2.3×10^2
		544 (sh)	1.9×10^2
		443	3.0×10^3
		413	2.3×10^3
		347	5.0×10^3
		300 (sh)	2.9×10^3
		221	4.8×10^3
III[e]	3:1	638 (sh)	5.2 × 10
		593	6.3 × 10
		447	1.9×10^2
		416 (sh)	2.0×10^2
		294	2.2×10^3, 6.6×10^3 [f]
IV[e]	3:1	598	3.9 × 10
		443 (sh)	8.1 × 10
		293	2.8×10^3, 8.4×10^3 [f]

[a] Measured at 5 °C by using a scan rate of 1 nm/s. Uncertainty in extinction coefficients is ca. ±5%. [b] Expressed per mole of Cr, unless otherwise stated. [c] Eluted with 1 M $LiClO_4$–0.1 M $HClO_4$. [d] Eluted with 1 M $LiClO_4$. [e] Eluted with 2 M $LiClO_4$–0.1 M $HClO_4$. [f] Expressed per mole of hydroquinone.

The UV–visible spectrum of complex II contains broad bands with maxima at 632 and 587 nm, shoulders near 544 and 300 nm, and sharp, intense bands with maxima at 443, 413, 347, and 221 nm. In addition, poorly resolved shoulders near 665 and 685 nm were noted in spectra of concentrated solutions. The absorption spectrum of complex II in strongly acidic solution (0.1 M $HClO_4$) could not be obtained even at 5 °C, as decomposition to $Cr(H_2O)_6^{3+}$ is fast on the time scale of the spectral measurement under these conditions. When eluted with 1 M $LiClO_4$, complex II was stabilized sufficiently to permit the measurement of a reproducible UV–visible spectrum (Figure 1). It should be noted that no differences in the positions and relative intensities of the principal absorption bands were found on comparing spectra of complex II in 1 M $LiClO_4$ and in 1 M $LiClO_4$–0.1 M $HClO_4$.

As complex III was eluted with 2 M $LiClO_4$–0.1 M $HClO_4$, the golden yellow component still was not moved from the top of the column. The Cr:H_2Q ratio in complex III is 3 (2.9 ± 0.2):1; this fraction contained 15% of the chromium in the product mixture. Recovery of 96% of the total chromium thus was achieved by collecting the $Cr(H_2O)_6^{3+}$ band and the complex I–III fractions. Recovery of organics (hydroquinone + benzoquinone) from the column was within experimental error of 100%. The UV–visible spectrum of complex III shows an asymmetric, broad band with maximum at 593 nm and a shoulder near 638 nm; the remaining spectral features include a comparatively narrow band with maximum at 447 nm, a shoulder near 416 nm, and a sharp, intense peak at 294 nm.

The products described above were still found when the order of addition of the reactants was reversed. Thus, 0.60 mmol of BQ in 25 mL of water was slowly added to 0.575 mmol of Cr(II) in a solution prepared by injecting 1.25 mL

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(6) Deutsch, E.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1532–44.
(7) Laswick, J.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3564–7.

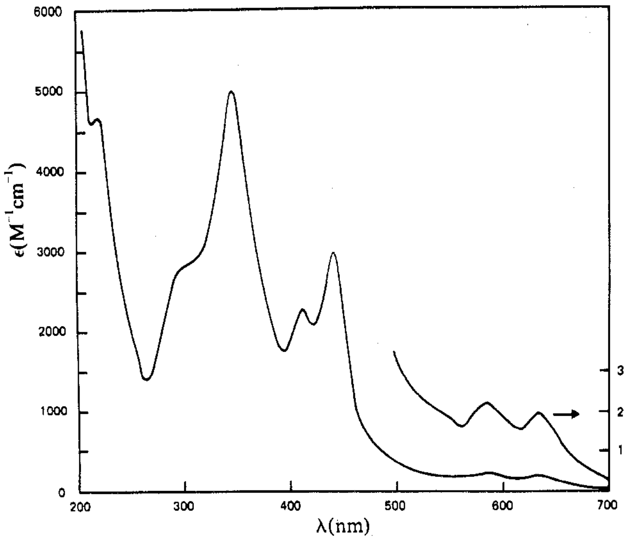

Figure 1. UV-visible absorption spectrum of $[(H_2O)_5CrOCr(H_2O)_5]^{4+}$ (complex II); 5 °C, 1 M $LiClO_4$ solution, [Cr] = 1.9×10^{-4} M. Extinction coefficients are expressed per mole of Cr. The spectrum was recorded on a Cary 17 spectrophotometer, scanning at 1 nm/s.

of 0.460 M $Cr(ClO_4)_2$–0.117 M $HClO_4$ into 25 mL of water. No attempt was made to precisely quantitate the distribution of chromium among the several components eluted from a 15 × 2.5 cm SP-C-25 column in this experiment, but it was observed that the products were identical with those described above and that the relative yields of $Cr(H_2O)_6^{3+}$ and complexes I–III were essentially independent of the order of addition of the reactants.

II. Addition of Cr^{2+}(aq) to Benzoquinone in 0.1 M $HClO_4$. Product distribution studies were also carried out for the reaction of 1.25 mL of 0.460 M $Cr(ClO_4)_2$–0.117 M $HClO_4$ with 0.60 mmol of BQ in 50 mL of 0.112 M $HClO_4$. The chromous solution was slowly added to the benzoquinone at 0 °C, yielding a dark yellow-brown solution. The product mixture was immediately absorbed onto a 15 × 2.5 cm cation-exchange column, and free organics were collected by elution with 0.1 M $LiClO_4$–0.1 M $HClO_4$. Under these conditions, 82% of the hydroquinone produced was found free in solution.

The distribution of chromium-containing products from the reaction of Cr(II) with acidic BQ is markedly different from that obtained with BQ dissolved in pure water. Elution with 1 M $LiClO_4$–0.1 M $HClO_4$ brought the blue-violet $Cr(H_2O)_6^{3+}$ band off the column quickly, leaving a green band with a diffuse yellow–green leading edge. The blue-violet band accounted for 75% of the chromium in the product mixture but only 1% of the total H_2Q. Further elution with 1 M $LiClO_4$–0.1 M $HClO_4$ caused the green band to split into closely spaced olive green (leading), yellow-brown, and emerald green (trailing) components. The leading component, containing 3% of the total Cr, exhibited a UV–visible spectrum identical with that of complex I. The yellow-brown fraction eluted next (2% of the total Cr) was identified as complex II on the basis of its UV–visible spectrum. As complex II was being eluted, the only remaining band (emerald green) had moved two-thirds of the way down the column. This emerald green cation (complex IV) was eluted with 2 M $LiClO_4$–0.1 M $HClO_4$. Complex IV exhibits a UV–visible spectrum quite similar to that of complex I (a broad, weak band with a maximum at 598 nm, a shoulder near 443 nm, and an intense absorption with λ_{max} at 293 nm) but contains chromium and hydroquinone in a 3 (2.9 ± 0.1):1 ratio. Recovery of 99% of the chromium in the product mixture was attained in this experiment, as 19% of the total Cr was eluted in the emerald green band.

An experiment analogous to that described in I above showed that the products obtained and relative yields in the reaction of Cr^{2+}(aq) with acidic BQ are not changed upon reversing the order of addition of the reactants. The low yield of complex II obtained from the chromatographic separation of the products of this reaction is somewhat misleading, as visible spectra recorded within 5 min after mixing showed that 35–40% of the chromium(III) initially appeared as complex II. By contrast, spectra of the solution obtained by adding Cr^{2+}(aq) to BQ in pure water indicated that the predominant initial products were, in this case, $Cr(H_2O)_6^{3+}$ and complex I. Finally, although nearly 100% of the chromium in the product mixture was retained on the cation-exchange column, the initial eluate containing BQ and free H_2Q was passed through a short DEAE-Sephadex A-50 anion-exchange column to determine whether any anionic chromium products (i.e., $Cr_2O_7^{2-}$, $HCrO_4^-$) were present. No such products were found.

III. Thermal and Oxidative Hydrolysis of Complexes I–IV. On standing at room temperature, complexes I–IV all undergo hydrolysis in acidic solution to give $Cr(H_2O)_6^{3+}$ as the exclusive chromium product. In the presence of 0.1 M $HClO_4$, hydrolysis of complexes I and IV was found to be complete within 2–3 days. Hydrolysis of complex III is significantly faster, proceeding to completion on overnight standing at room temperature. Preliminary kinetic observations on the hydrolysis of complex II (followed spectrophotometrically at 347 nm) showed that the half-life of this reaction is ca. 1.5 h in 0.1 M $HClO_4$ (μ = 1.0 M ($LiClO_4$), 25 °C); these kinetic results also confirmed that the rate of complex II hydrolysis increases with increasing $[H^+]$. While complex II hydrolyzes much faster than complex I in acidic solution, complex I is more susceptible to hydrolysis when absorbed on SP-C-25 resin at 5 °C. Thus, essentially complete hydrolysis of complex I to $Cr(H_2O)_6^{3+}$ occurred upon standing overnight in the resin phase, but complex II could be retained on cation-exchange columns for several days at 5 °C.

Spectra of the complex I fraction measured 4–6 days after elution and storage at 5 °C showed that this species slowly converts to complex II at low temperature. Thus, the broad, weak 603-nm band of complex I was slowly replaced by the more intense spectral features at 632, 587, 443, and 413 nm characteristic of complex II. After prolonged storage of the eluate solution at 5 °C, the complex II spectrum ultimately was replaced by the weak bands at 408 and 574 nm characteristic of $Cr(H_2O)_6^{3+}$.

Treatment of complex I with ceric perchlorate solution to oxidize hydroquinone caused its instantaneous conversion to complex II, with liberation of benzoquinone into solution. Thus, the distinctive absorption spectrum of complex II was observed immediately following the addition of several drops of 0.5 N Ce(IV) in 6 N $HClO_4$ to 3 mL of freshly eluted complex I solution in a spectrophotometer cell. Complex II and $Cr(H_2O)_6^{3+}$ were the only chromium products observed in the chromatographic separation of the mixture resulting from the addition of a slight excess of Ce(IV) to complex I; the organic product was, as expected, 1,4-benzoquinone. The complex II absorption spectrum was also observed immediately following the addition of ceric perchlorate solution to complex IV, but similar treatment of complex III resulted only in the bleaching of the visible absorption spectrum; the immediate Cr(III) products resulting from the Ce^{IV}–complex III reaction have not yet been elucidated.

IV. Attempted Determination of Ionic Charges. An attempt was made to measure the charge per chromium atom for complexes I–IV by using the ion-exchange method of Cady and Connick.[8] Complexes absorbed on H^+-form SP-C-25

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(8) Cady, H. H.; Connick, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 2646–52.

columns were eluted with 0.098 M $Ce(ClO_4)_3$–0.058 M $HClO_4$ solution, and the H^+, Ce(III), and Cr(III) content of the eluate solutions were assayed by standard methods.[6,8] Reproducible results were not obtained for any of the complexes under consideration except $Cr(H_2O)_6^{3+}$. Indeed, elution of complexes I and IV with acidic Ce(III) invariably yielded solutions contaminated with complex II, suggesting that the former two species are activated toward hydrolysis under the experimental conditions. This was confirmed by showing that the addition of $Ce(ClO_4)_3 \cdot 6H_2O$ to complex I or IV solutions resulted in the rapid formation of some complex II, with the rate and extent of this conversion increasing with increasing [Ce(III)].

The elution behavior of complexes I and II on SP-C-25 resin is consistent with that expected for 4+ cations.[9] To test the hypothesis that these are in fact 4+ cations, we eluted a mixture of complex I, complex II, and $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ from a 16 × 3 cm cation-exchange column. The three components were not cleanly separated on elution with 1 M $LiClO_4$–0.1 M $HClO_4$. Spectra of the fractions eluted from this column showed, however, that the order of elution was complex I, $[(H_2O)_4Cr(OH)_2Cr(H_2O_4]^{4+}$, and complex II.

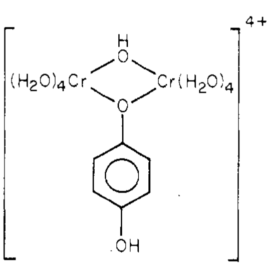
Discussion

Oxidation of Cr^{2+}(aq) by many two-electron oxidizing agents (i.e., HClO, H_2O_2) leads to the formation of a binuclear product,[3] $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$,[10] plus some $Cr(H_2O)_6^{3+}$. A striking feature of our product distribution studies, therefore, is that none of the dihydroxo-bridged chromium dimer was found in the reaction of Cr(II) with benzoquinone in either weakly or strongly acidic solution. The mechanism proposed by Ardon and Plane[3] for the formation of the di-μ-hydroxo-bis(tetraaquochromium(III)) ion is: Cr^{II} + two-electron oxidizing agent → Cr^{IV}; $Cr^{II} + Cr^{IV} \rightarrow$ binuclear product. Our product distribution results therefore imply that Cr(IV) is not produced as an intermediate in the Cr^{II}–BQ reaction. Indeed, this must be so considering that no $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ was obtained even when BQ was added to a solution containing an initial excess of Cr(II). The formation of Cr(IV) in the Cr^{II}–BQ reaction almost certainly is thermodynamically unfavorable, as benzoquinone ($E° = +0.70$ V)[11] is a weak two-electron oxidant when compared with HClO ($E° = +1.49$ V)[11] and H_2O_2 ($E° = +1.77$ V).[11] Ardon and Plane attribute the low reactivity of Cr(II) with H_3AsO_4 ($E° = +0.56$ V),[11] a two-electron oxidant comparable in strength to BQ, to the thermodynamic inaccesibility of Cr(IV) in this system.[3]

The most interesting product obtained from the Cr^{II}–BQ reaction is complex II, a species whose visible spectral features differ markedly from the weak, broad d–d bands typically encountered[12] in the spectra of chromium(III) complexes. Complex II clearly cannot be a chromium(III)–hydroquinone species in view of the absence of H_2Q in this fraction and the observation that complex II is produced through the oxidation of hydroquinone present in complexes I and IV. Complexes I and II elute so close to $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ on SP-C-25 resin that it seems reasonable to conclude that all of these ions carry a charge of 4+.

The near-ultraviolet absorption spectrum of complex II, proposed to be $[(H_2O)_5CrOCr(H_2O)_5]^{4+}$, strongly resembles that of the "basic rhodo" chromium(III) ion $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$. Thus, the three intense absorption bands at 443 (22 570 cm^{-1}), 413 (24 210 cm^{-1}), and 347 nm (28 820 cm^{-1}) correspond closely in both sharpness and relative intensity to those of the "basic rhodo" ion[13] at 25 160, 26 490, and 29 850 cm^{-1}, respectively. Several theoretical descriptions of the exchange interaction in oxo-bridged chromium(III) complexes have been presented,[13-17] but the assignment of the electronic absorption spectrum of $[(NH_3)_5Cr]_2O^{4+}$ remains considerably uncertain.[17] While we are not presently prepared to attempt the assignment of complex II's electronic spectrum, it seems clear that such unusually narrow and intense near-ultraviolet features are associated specifically with the Cr–O–Cr structural unit. Thus, the visible spectra of hydroxo- ($[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$)[13] and dihydroxo-bridged (i.e., $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$)[7] binuclear chromium(III) ions contain only the weak, broad, spin-allowed d–d bands expected for the d^3 configuration. The distinctive spectral features of the "basic rhodo" ion apparently result from perturbations in the electronic structure of Cr(III) owing to strong π bonding in the linear Cr–O–Cr group.[13]

The structure of complex I most likely is



considering its chromium to hydroquinone ratio, elution behavior, facile oxidative conversion to complex II, and spectral similarity to the di-μ-hydroxo-bis(tetraaquochromium(III)) ion. Thus, the Ce(IV)-induced transformation of complex I to complex II is readily accounted for in terms of a process involving the oxidation of coordinated hydroquinone followed by loss of benzoquinone into solution (eq 2). The observed

$$[(H_2O)_4Cr(OH)(HQ)Cr(H_2O)_4]^{4+} + 2Ce^{IV} + 2H_2O \rightarrow [(H_2O)_5CrOCr(H_2O)_5]^{4+} + 2Ce^{III} + BQ + 2H^+ \quad (2)$$

thermal and oxidative transformations of complex I to complex II clearly rule out the assignment of complex I as $[(H_2O)_5CrOC_6H_4OCr(H_2O)_5]^{4+}$. The visible spectral features of complex I at 603 and near 440 nm are red-shifted relative to those of $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ ($\lambda_{max} = 418$ nm ($\epsilon = 22.5$ M^{-1} cm^{-1}), 582 nm ($\epsilon = 18.9$ M^{-1} cm^{-1}))[7] by ca. 20 nm. With assignment of the long-wavelength band as ${}^4A_{2g} \rightarrow {}^4T_{2g}(O_h)$, it is seen that $10Dq$ for complex I (16 580 cm^{-1}) is smaller than that of the dihydroxo-bridged dimer by 600 cm^{-1}. Such a decrease in $10Dq$ is expected, as the phenolate anion HQ^- presumably is a more effective π-donor ligand than OH^-, placing it lower in the spectrochemical series. The intense bands found between 290 and 300 nm in the ultraviolet spectra of complexes I, III, and IV most likely correspond to a hydroquinone-to-chromium(III) charge-transfer transition ($2b_{2g} \rightarrow e_g(\sigma^*)$). The intensities of these bands are substantially larger than would be expected for the symmetry-forbidden ${}^1A_{1g} \rightarrow {}^1B_{1u}$ electronic transition[18] of the benzene nucleus, also occurring near 300 nm in hydroquinone derivatives (for HQ^-, $\lambda_{max} = 307$ nm ($\epsilon = 2.75 \times 10^3$ M^{-1} cm^{-1})).[4]

Complex I might reasonably be formed through an electron-transfer pathway involving concerted attack of two Cr^{2+}(aq) ions at one of the benzoquinone oxygen atoms, forming a doubly bridged precursor complex (eq 3). Such

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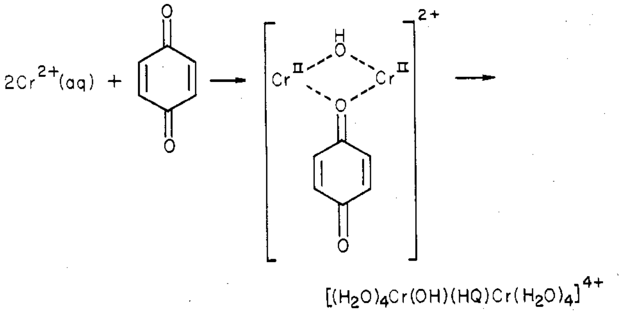
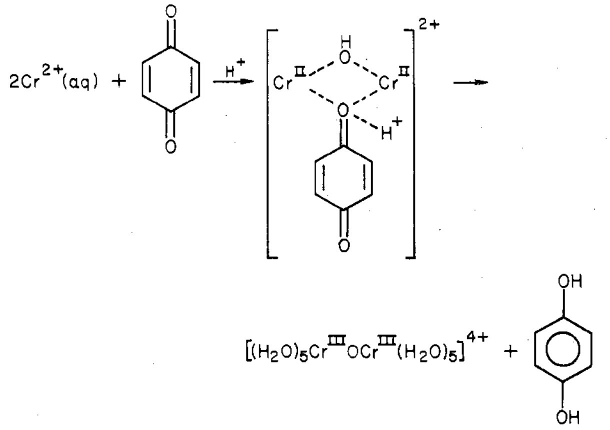


(3)

I

a precursor complex could be strongly stabilized by multiple bonding between the high-spin d^4 Cr(II) centers, analogous to that observed in chromous acetate, $Cr_2(O_2CCH_3)_4(H_2O)_2$, a binuclear compound possessing four acetate bridges between the quadruply bonded chromium atoms.[19] By contrast, similar stabilization of the precursor complex would not be expected in the formation of another 2:1 chromium(III)–hydroquinone complex, $[(H_2O)_5CrOC_6H_4OCr(H_2O)_5]^{4+}$, perhaps accounting in part for the absence of this product in the Cr^{II}–BQ reaction.

Complex I undergoes very slow hydrolysis in acidic solution at room temperature, indicating that this product is not a precursor of complex II under our conditions for the reaction of Cr^{2+}(aq) with benzoquinone. The initial yield of complex II was found to be maximal when the reaction was carried out in strongly acidic solution, suggesting that the oxo-bridged complex may be formed through the oxidation of chromous ion by protonated benzoquinone, BQH^+, followed by rapid loss of hydroquinone into solution (eq 4). This hypothesis would also account for the comparatively low yield of complex I obtained from the reaction of Cr(II) with BQ in 0.1 M $HClO_4$. While the ionization constant of BQH^+ is not known with certainty, prewaves observed in the polarographic reduction of benzoquinone in perchloric acid media clearly point to the existence of this species.[20]



(4)

The $Cr(H_2O)_6{}^{3+}$ ion was found to be a major product in the reaction of Cr^{2+}(aq) with BQ. While some $Cr(H_2O)_6{}^{3+}$ undoubtedly results from the hydrolysis of complex II, particularly in strong acid, not enough complex II was observed initially in product mixtures to account for all of the $Cr(H_2O)_6{}^{3+}$ recovered in the cation-exchange experiments. The $Cr(H_2O)_6{}^{3+}$ not formed through the hydrolysis of complex II probably comes from the outer-sphere one-electron reduction of BQ, producing benzosemiquinone, which then rapidly disproportionates into H_2Q and BQ. It is estimated that this outer-sphere pathway accounts for at least 30% of the chromium(III) product of the Cr^{II}–BQ reaction in both weakly and strongly acidic solutions. It should be noted that small, but definite, amounts of hydroquinone (1% of total H_2Q) were found in the $Cr(H_2O)_6{}^{3+}$ fraction, suggesting the presence of a Cr^{III}–H_2Q complex with a 3+ charge (perhaps $[(H_2O)_5Cr(H_2Q)]^{3+}$). The possibility that this complex is an intermediate hydrolysis product of complex I, III, or IV is currently being investigated.

Perhaps the most surprising result of our product distribution studies is the finding of two trinuclear chromium(III)–hydroquinone products, complexes III and IV. Such products certainly would not be expected in the reaction of Cr(II) with a two-electron oxidant. Our results on the stoichiometry, elution behavior, spectra, and reactivity of complexes III and IV do not provide a basis for definitively assigning the structures or charges of these species. The elution behavior of these complexes, however, suggests charges of 5+ or 6+. It may also be noted that the UV–visible spectra of complexes I and IV are quite similar and that both of these cations are converted to complex II upon oxidative hydrolysis of coordinated hydroquinone. On this basis it seems likely that both complexes contain the doubly bridged [Cr(OH)(HQ)Cr] structural unit.

The visible absorption spectrum of complex III, like that of complex II, cannot be assigned simply in terms of the d–d transitions arising from the d^3 configuration in a near-octahedral crystal field. Thus, at least four moderately strong electronic transitions occur between 650 and 400 nm, while only two d–d bands (${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4T_{1g}(F)$) are observed within this interval in the spectra of $Cr(H_2O)_6{}^{3+}$, complex I and complex IV. The larger number of transitions in the complex III spectrum probably reflects a low-symmetry field component, resulting in the splitting of the ${}^4T_{2g}$ and ${}^4T_{1g}$ octahedral crystal field states. Complex III undergoes hydrolysis significantly faster than complexes I and IV and, unlike the latter two cations, is not converted to $[(H_2O)_5CrOCr(H_2O)_5]^{4+}$ upon treatment with Ce(IV). On this basis we conclude that the [Cr(OH)(HQ)Cr] structural unit is not present in complex III; perhaps this trinuclear product is held together through single OH bridges between the chromium atoms. The formation of trinuclear chromium(III) products in the Cr^{II}–BQ reaction implies the existence of electron-transfer pathways requiring the formation of polynuclear precursor complexes. The structures and origins of these interesting species are still under investigation.

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Registry No. I, 73360-43-7; II, 73347-70-3; $Cr(H_2O)_6{}^{3+}$, 14873-01-9; Cr(II), 22541-79-3; benzoquinone, 106-51-4.

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