trifurcated ("J" = 0.75) and almost equal outer spikes 7.03 s^{-1} apart.

For $CF_3P(CHF_2)_2$, the ^{19}F spectrum lacks apparent complexity: there are only four slightly irregular clusters. Comparison of cluster widths in the XL100 and WP270 spectra shows that the $\Delta\delta$ for an AB spectrum cannot exceed 0.3 ppm; then R cannot exceed 0.0005. But the ^{31}P spectrum does show two values for J_{PCF}, proving that P couples to equivalent pairs of magnetically nonequivalent F atoms. Thus there is at least AB complexity, but with the A and B fluorine atoms almost perfectly superposed. The ^1H spectrum consists of four unsymmetrical triplets for which J_{HCPCF} is near 4.5; more than AB complexity is suggested, but the fine structure is not resolved well enough for analysis.

The adventitious product $P(CHF_2)_3$ was seen first in the ^{19}F spectrum (XL100 instrument), 0.1818 ppm upfield of $CF_3P(CHF_2)_2$, neatly interlaced without superposition of any peaks. The present data are for a pure sample made by the P_4–CHF_2I reaction, yet to be described. Omitted from Tables VI and VIII are $_5J_{HCPCF} = 4.3$ and $_3J_{FCPCH} = 4.25$, confirming that these are J values suitable for use in computer simulation of other $RP(CHF_2)_2$ spectra. This is far stronger coupling than ever before seen for HCPCF chains.

The ^{19}F spectrum of $CH_3OP(CF_3)CHF_2$ (recorded for an authentic sample) would have interlaced with or superposed upon $CH_3OP(CHF_2)_2$, but no sample from the dimer methanolysis ever showed any trace of such confusion.

Acknowledgment. I am grateful to the operators of the XL200 and WM500 instruments for some of the NMR spectra and to Dr. K. L. Servis for aid with difficult interpretations.

Registry No. $CH_3O(CF_3)PCF_2P(CF_3)CHF_2$ (isomer I), 94110-48-2; $CH_3O(CF_3)PCF_2P(CF_3)CHF_2$ (isomer II), 94110-49-3; HCF_3, 75-46-7; $(CH_3O)_3P$, 121-45-9; $CF_3P(CHF_2)_2$, 94110-50-6; $CH_3OP(CHF_2)_2$, 94110-51-7; $(CH_3O)_2PCF_2P(CF_3)CHF_2$, 94110-52-8; *cis*-$(CF_3PCF_2)_2$, 86350-48-3; *trans*-$(CF_3PCF_2)_2$, 86350-50-7; MeOH, 67-56-1; $(CH_3O)_2PCHF_2$, 4669-85-6; $P(CHF_2)_3$, 94110-53-9; $CHF_2(CF_3)PCH_2P(CF_3)Cl$, 94110-54-0; $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ (isomer I), 86350-51-8; $CH_3(CF_3)PCF_2P(CF_3)CHF_2$ (isomer II), 86350-52-9; $ClP(CHF_2)_2$, 94110-56-2; $(CH_3)_2NP(CHF_2)_2$, 94110-57-3.

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Ethanol Oxidation by Chromium(III) Complexes of Chloranilic Acid. Spectroscopic, Electrochemical, Magnetic, and Chromatographic Studies of Chloranilate Semiquinone-Bridged Polynuclear Chromium Ions

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The oxidation of ethanol by chloranilic acid (H_2CA_{ox}; 2,5-dihydroxy-3,6-dichlorobenzoquinone), catalyzed by Cr(III), has been reexamined. Rate and spectrophotometric studies showed that a binuclear complex of the form $Cr_2(CA_{ox})^{4+}$ is the most reactive catalyst species; reduction of $Cr_2(CA_{ox})^{4+}$ is first order with respect to ethanol (95–99%), with a rate constant of 1.5×10^{-3} M^{-1} s^{-1} (60 °C). Spectrophotometric, chromatographic, magnetic susceptibility, electron paramagnetic resonance, and cyclic voltammetric measurements on the reduced chloranilate- (CA_r-) containing catalyst reduction product are also reported. Both 2:1 (I) and 5:2 Cr–CA_r complexes, with intense absorption maxima at 300, 355, 428, 458, 494, 600, and 654 nm, are formed in ethanol/water solutions. Binuclear complex I in 99% ethanol exhibits an effective magnetic moment per Cr atom of 3.81 μ_B (298.2 K), near the spin-only value for three unpaired electrons, an EPR resonance at $g = 1.97$ (100 K), and a quasi-reversible cyclic voltammogram (0.1 M $(n\text{-}C_4H_9)_4NClO_4$, 25.0 °C) indicative of a two-electron oxidation with $E_{1/2} = +0.46$ V vs. SCE. Cation-exchange separations on SP-Sephadex C-25 resin confirmed the stoichiometry of I and demonstrated that its immediate oxidation product rapidly decays to give $Cr(H_2O)_6^{3+}$ and a 1:1 complex ($Cr(CA_{ox})^+$) in aqueous acidic solution. The 400–500-nm spectra of I and the chloranilate semiquinone trianion radical ($CASQ^{3-}$) are remarkably similar, suggesting that the predominant resonance form of I is Cr(II)–bridging $CASQ^{3-}$–Cr(III) rather than Cr(III)–bridging chloranilate hydroquinone–Cr(III). Qualitative molecular orbital arguments are presented to reconcile the magnetic results with this hypothesis and account for the electronic spectra of $CASQ^{3-}$ and I.

Introduction

Benzoquinones with electron-withdrawing substituents, such as chloranil (tetrachloro-1,4-benzoquinone), are versatile two-electron oxidants in organic synthesis.[1] Quinones are prime candidates as electron acceptors in alcohol-oxidizing fuel cell catalysts, as the electrochemical reversibility of most quinone/hydroquinone couples is excellent.[2] Furthermore, the capability of certain activated quinones to convert alcohols into the corresponding carbonyl compounds is already documented.[3,4] The catalytic potential of benzoquinones is considerably enriched through the coordination of these ligands to transition-metal ions.[5] For example, iron–quinone complexes serve as efficient electron carriers in mitochondria and in bacterial photosynthetic systems.[6,7]

An intriguing report by Linck and Taube suggests that chromium(III) complexes of 2,5-dihydroxy-1,4-benzoquinone (H_2DHBQ) and chloranilic acid (H_2CA, 2,5-dihydroxy-3,6-dichloro-1,4-benzoquinone) may serve as ethanol oxidation catalysts under mild conditions (25 °C), yielding acetaldehyde as the sole organic product.[8] Acetaldehyde is formed more rapidly through the action of strong transition-metal oxidants (i.e. MnO_4^-, $Cr_2O_7^{2-}$) on ethanol in aqueous solution,[9] but the electrochemical irreversibility of these oxidants prevents their use as catalysts. Furthermore, most of the free energy released in the C_2H_5OH–O_2

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reaction would be dissipated through the intermediacy of a strongly oxidizing catalyst, leaving a small fraction of the overall free energy change to be translated into useful work in a fuel cell. The feasibility of catalytic ethanol oxidation involving a thermodynamically weak two-electron acceptor is clearly demonstrated by the Zn-containing metalloenzyme liver alcohol dehydrogenase, in which NAD^+ (nicotinamide adenine dinucleotide) is rapidly reduced to NADH.[10]

A primary goal of our research is to develop transition-metal complexes of chloranilic acid and related hydroxybenzoquinones as ethanol and acetaldehyde oxidation catalysts. A brief review of the known coordination chemistry of dihydroxybenzoquinones will therefore be given. Acid ionization of both chloranilic acid OH groups occurs in aqueous solution ($pK_1 = 0.76$, $pK_2 = 2.58$; 25 °C, $I = 0.5$ M);[11] the chlorine and hydroxy substituents reduce the two-electron-oxidizing strength of chloranilic acid ($E° = 0.449$ V in 1 N HCl, 25 °C)[12] as compared with that of 1,4-benzoquinone (0.699 V).[2] Although many coordination compounds of chloranilic acid and 2,5-dihydroxybenzoquinone have been reported, most are polymeric, poorly characterized materials. Early workers in this area pointed out that 2,5-dihydroxy-1,4-benzoquinones may be considered as stabilized enols of 1,2-diketones, facilitating the formation of five-membered chelate rings with metal ions.[13] The preparations of numerous bivalent transition-metal–chloranilate complexes have been described,[14] but the water insolubility of many such complexes has hindered their thorough characterization. Nevertheless, perturbations in the 500–600-nm absorbance of chloranilic acid have been utilized to define the composition and formation constants of 1:1 (Ni(II)) and 2:1 (Fe(III)) CA–transition-metal complexes in aqueous solution.[15]

The X-ray crystal structures and magnetic susceptibilities of binuclear Ni(II) and Cu(II) complexes with CA^{2-} and $DHBQ^{2-}$ bridging groups have been reported.[16] In these complexes, polymerization was prevented by blocking the coordination positions not occupied by quinone oxygen atoms with polydentate amine ligands. The crystal structures of $[Ni_2(tren)_2(CA)](BPh_4)_2$ and $[Cu_2(Me_2dien)_2(CA)](BPh_4)_2$ show that each metal atom is chelated by 1,2 or 4,5 pairs of chloranilate oxygen atoms. The bridging chloranilate dianion is planar and has a localized quinonoid structure with four very short and two long (single) C–C bond lengths.[16] Weak antiferromagnetic coupling between the metal centers ($J = -1.8$ cm^{-1}), mediated by the chloranilate bridge, was observed in the nickel dimer.[16] Similar antiferromagnetic coupling exists in the CA^{2-}- and $DHBQ^{2-}$-bridged iron(III) dimers $Fe_2(DHBQ)_3(H_2O)_4$ and $Fe_2(CA)_3(H_2O)_4 \cdot 4H_2O$.[17]

Linck and Taube discovered the chromic ion catalyzed oxidation of ethanol by H_2CA and H_2DHBQ and reported that the former reaction exhibits a half-life of ca. 15 min at 25 °C in the presence of a large excess of chromic ion.[8] Binuclear chromium(III) products bridged by the hydroquinone analogues of $DHBQ^{2-}$ and CA^{2-} were postulated on the basis of spectrophotometric evidence. We report here rate studies of ethanol oxidation by chromium(III)–chloranilate complexes, coupled with spectrophotometric, chromatographic, magnetic susceptibility, electron paramagnetic resonance, and cyclic voltammetric measurements on the polynuclear chromium product. While our observations are in essential agreement with the pioneering study,[8] some important, unsuspected aspects of the chromium(III)–chloranilate–ethanol system are described in this paper. In particular, facile ethanol oxidation occurs only in solutions where $[Cr(III)]_{tot} > [CA]_{tot}$ and the polynuclear chromium product contains a bridging chloranilate semiquinone trianion radical rather than the hydroquinone tetraanion.

Experimental Section

Materials. Reagent grade chemicals were used throughout. Solutions were prepared from triply distilled water and absolute ethanol dried over molecular sieves. $Cr(ClO_4)_3 \cdot 6H_2O$ (G. F. Smith) and chloranilic acid (Sigma) were used as received. Stock solutions of chromous perchlorate were prepared through the anaerobic (N_2 atmosphere) reduction of acidic $Cr(ClO_4)_3$ over 2% zinc amalgam.

Analyses. Chromium was assayed spectrophotometrically by the basic peroxide method.[18] Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Cation-exchange chromatographic separation of chromium complexes was accomplished on SP-Sephadex C-25 resin, with aqueous $LiClO_4$–$HClO_4$ solutions as eluants.[19] As the chromium product of Cr(III)–CA-catalyzed ethanol oxidation is susceptible to aerobic oxidation in aqueous solution, the stoichiometry of this complex was obtained from an anaerobic cation-exchange experiment. A 20 × 2 cm column was equilibrated with 600 mL of N_2-purged water. A 1-mL aliquot of 4.44×10^{-2} M $Cr(ClO_4)_3$ equilibrated with 2.22×10^{-2} M H_2CA in 99% ethanol was diluted to 100 mL in water and applied to the column with continuous N_2 purging. Upon elution with anaerobic 0.5 M $LiClO_4$–0.001 M $HClO_4$, a purple leading band was well separated from a predominant light green component (I) with a UV–visible spectrum in good agreement with that of the ethanolic Cr(III)–CA product solution. Aerobic oxidation of I readily afforded $Cr(H_2O)_6^{3+}$ and the purple 1:1 Cr(III)–CA ion (vide infra), but quantitative release of the quinone ligand from Cr could not be achieved even upon prolonged boiling of the latter species in acidic solution. The chloranilate content of I was therefore determined from the ultraviolet absorbance of the $Cr(CA)^+$ aerobic oxidation product ($\epsilon_{332}(\max) = 1.42 \times 10^4$ M^{-1} cm^{-1}). On this basis, the light green band, with a Cr:CA ratio of 2.1 ± 0.1, accounted for 96% of the chromium eluted from the column; 100% of the chromium added to the column was recovered in the two bands.

Isolation of a Solid from Ethanolic Solutions of I. Several approaches were examined toward the isolation of solids from dark green, concentrated ethanolic solutions of $Cr(ClO_4)_3 \cdot 6H_2O$ equilibrated with H_2CA in an exactly 2:1 stoichiometric ratio. Solids were not obtained through the addition of cation precipitation reagents such as $NaBPh_4$ and $N(n\text{-}C_4H_9)_4PF_6$ in large excess. Slow evaporation of ethanol gave purple gums heavily contaminated with oxidation products.

A solid with properties similar to the green parent solution was isolated following the rapid removal of most of the solvent at 50–60 °C on a rotary evaporator. Residual water and ethanol were extracted from the resultant dark green oil by resuspension in benzene, followed by rotary evaporation of the solvent. Crystallization of the thick oily residue could not be induced by resuspension in chloroform, ethyl ether, or acetone, with subsequent cooling in an ice bath.

Slow addition of ethyl ether to an acetone solution of the green complex saturated with $NaBPh_4$ gave a gummy green-brown precipitate. This solid was collected on a sintered glass filter and washed extensively with ether, affording the removal of coprecipitated $NaBPh_4$ in a pale yellow supernatant. The resultant brown-green powder (II) was dried in vacuo. Unfortunately, II could not be dissolved in water, methanol, ethanol, chloroform, or acetone but did dissolve, with decomposition, in 0.1 M $HClO_4$.

Anal. Calcd for $Na_{13}Cr_5(CA)_2(OH)_{13}(H_2O)_{17}(ClO_4)_9$ ($Cr_5C_{12}H_{47}Cl_{13}Na_{13}O_{74}$): C, 6.02; H, 1.98; Cl, 19.24; Cr, 10.85; Na, 12.48. Found: C, 6.05; H, 1.52; Cl, 19.05; Cr, 10.91; Na, 12.07. IR (KBr pellet): 3400 (s, br), 1610 (m), 1525 (m), 1430 (w), 1370 (m), 1250 (vw, sh), 1080 (vs; 1100 and 1130, sh), 940 (w), 850 cm^{-1} (m).

Kinetic Measurements. Anaerobic ethanol oxidation rates were evaluated from absorbance–time traces at 493 nm, where the reduced chloranilate–chromium complex absorbs strongly. Instrumentation used in these slow rate measurements was as described previously.[20] Anaerobic (purged with ethanol–saturated N_2) ethanolic solutions of $Cr(ClO_4)_3$ were mixed with chloranilic acid (limiting reagent, 0.04 mM) in serum-capped 1 cm path length cells using Hamilton gastight syringes. No attempt was made to maintain constant ionic strength in [Cr(III)] variation studies.

In most runs, pseudo-first-order rate constants (k_{obsd}) were derived from the linear least-squares slopes of ln $(A_\infty - A_t)$ vs. time correlations. Substantial uncertainties in A_∞ for very slow runs at comparatively low

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Table I. UV-Visible Spectral Data[a]

complex	λ_{max}, nm	ϵ,[b] $M^{-1}\,cm^{-1}$	R[c]
III	330	1.64×10^4	0.97 (0.07), 2.3 (0.2)
	501	1.3×10^3	
IV	300	7.5×10^3	1.96 (0.14)
	355	6.5×10^3	
	428	2.3×10^3	
	458	6.0×10^3	1.12 (0.04), 2.54 (0.04)
	494	1.71×10^4	1.03 (0.11), 2.55 (0.04)
	600	6.1×10^2	
	654	1.2×10^3	2.42 (0.13)

[a] 99% ethanol, ambient temperature. Complex IV extinction coefficients were derived from a 0.10 mM CA-0.60 mM Cr(III) solution (Figure 1), correcting for the background absorbance of excess Cr(III). [b] Expressed per mole of CA. [c] Cr:CA stoichiometric ratios derived from spectrophotometric titrations (see text). Standard deviations are shown in parentheses.

ethanol (<96%) or Cr(III) (<0.016 M) concentrations made it necessary to derive k_{obsd} from the Guggenheim analysis,[21] on the basis of at least 4 half-lives of the reaction. First-order analytical plots were based on at least 80% of ΔA_{493}, excluding initial, comparatively rapid absorbance increases owing to $Cr(CA)^+$ formation (vide infra). Reported rate constants and uncertainties reflect the average of three trials.

Physical Measurements. UV-visible spectra were recorded on Perkin-Elmer Lambda 5 or Cary 17 spectrophotometers. Infrared spectra were acquired on a Beckman Acculab 8 instrument.

The Evans NMR method[22] (Varian XL-100 spectrometer) was employed to determine the paramagnetic susceptibility of chromium in a 99% ethanolic solution containing 2.22×10^{-2} M H_2CA equilibrated with 4.44×10^{-2} M $Cr(ClO_4)_3$. Magnetic susceptibility calculations were based on the ethanol CH_3 proton resonance frequency (center line of triplet) in the presence, and absence, of chromium. The sample temperature was determined by the method of Van Geet,[23] and correction was made for the diamagnetic susceptibility of the solvent.[24] Electron paramagnetic resonance spectra of powders and frozen solutions were obtained with a Varian E-109 spectrometer interfaced to a Hewlett-Packard 9835B microcomputer.

Cyclic voltammograms were generated with a Bioanalytical Systems CV-1B apparatus, and output was obtained from a Hewlett-Packard 7004 B X-Y recorder. A three-electrode system was used, composed of platinum-wire working and auxiliary electrodes in conjunction with an aqueous saturated calomel reference electrode. Frequent cleaning of the Pt working electrode[25] was necessary in order to obtain reproducible cyclic voltammograms of ethanolic solutions. Both aqueous and ethanolic solutions were purged with N_2 before the acquisition of voltammetric data.

Results

UV-Visible Spectrophotometric Titration. A UV-visible spectrophotometric titration was carried out by mixing various Cr(III) concentrations (0.025-1.00 mM) with 0.10 mM H_2CA in 99% ethanol. A rapid (complete within 30 min) color change from orange to purple (complex III; see Table I) was noted in all cases. In solutions containing more than a 1:1 mole ratio of Cr to chloranilate, subsequent slow formation of a yellow-green product (IV) was observed at room temperature. Although color development was nearly complete within 1 day, spectra were recorded 2 weeks after mixing to ensure that equilibrium had been reached.

In the region $[Cr]/[CA]_{tot} = 0.25$-1.00, decreases in the 300-nm absorbance of H_2CA were accompanied by increases in the 330- and 501-nm absorbance of the purple complex. As this ratio was varied from 1.00 to 6.00, the 330- and 501-nm bands were replaced by a series of intense transitions at 300, 355, 428, 458, 494, 600, and 654 nm (Figure 1A). Finally, as the ratio was increased from 6.0 to 10.0, further very small absorbance increases could be attributed to excess, unreacted Cr(III). No electronic absorption bands were observed between 800 and 2000 nm.

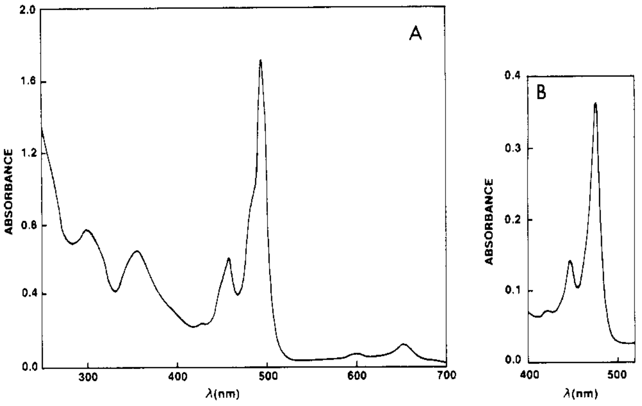

Figure 1. Absorption spectra of complex IV in 99% ethanol with [Cr] = 0.60 mM (A) and of chloranilate semiquinone in aqueous 6 M NaOH (B) ($[CA]_{tot}$ = 0.10 mM, room temperature, 1-cm path length). Chloranilate semiquinone was generated through the reduction of CA^{2-} by $Na_2S_2O_4$.[26] The spectrum in part B does not reflect quantitative conversion of chloranilate into the semiquinone.

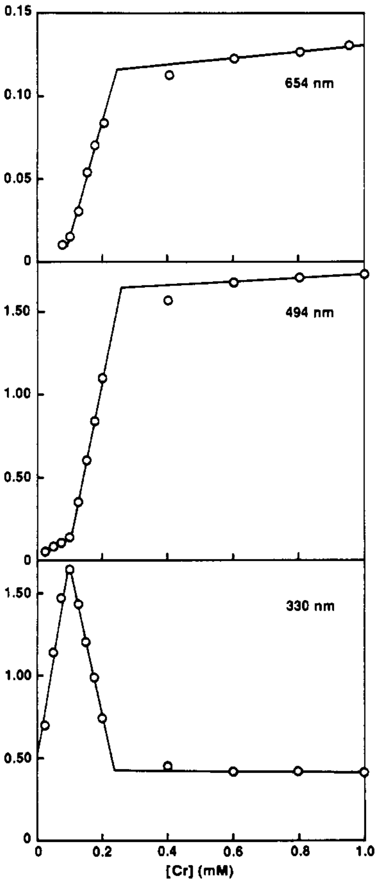

Figure 2. Spectrophotometric titrations of chloranilic acid with $Cr(ClO_4)_3$ in 99% ethanol ($[CA]_{tot}$ = 0.10 mM, room temperature, 1-cm path length).

Plots of A_λ vs. [Cr] at 300, 330, 458, 494, and 654 nm were constructed in order to derive the stoichiometries of the purple and yellow-green complexes from the spectrophotometric data. The 330-, 494-, and 654-nm results are shown in Figure 2. Stoichiometries are indicated by the discontinuity points in these diagrams, as measured by the intersection of linear least-squares lines that fit the A_λ-[Cr] profiles at low, intermediate, and high chromium concentrations. Table I presents UV-visible spectral data for III and IV along with Cr:CA ratios (R) based on these discontinuity points. At 300 nm, the absorbance decreases sharply to a minimum at $R = 2$ and then increases very slowly at higher [Cr]. We conclude, therefore, that two Cr atoms per H_2CA

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molecule are required to achieve full reduction of chloranilic acid.

The clear maximum in the 330-nm absorbance and the 458- and 494-nm discontinuity points at $R = 1$ demonstrate that III is a 1:1 complex of Cr(III) with chloranilic acid. Well-defined second breakpoints at $R = 2.5$ are seen in the titrations at 458 and 494 nm, the wavelengths where absorbance is most sensitive to complex IV concentration. Within experimental error, the 654-nm data support the $R = 2.5$ assignment; a somewhat lower value is apparent from the second breakpoint at 330 nm, where absorbance is more sensitive to [III]. We conclude that the thermodynamically favored redox product contains five Cr atoms per two molecules of reduced chloranilic acid when large excesses of Cr(III) over H_2CA are present. In this, we differ from the $R = 2$ (2.13) spectrophotometric titration result of Linck and Taube.[8]

Cation-Exchange Chromatography. Cation-exchange experiments were carried out to determine the products of the Cr^{2+}(aq)–H_2CA reaction, the oxidation products of IV, and to explore the existence of a 2:1 Cr(III)-reduced chloranilate (CA_r) complex, as previously reported.[8] Anaerobic aqueous chromatography of an ethanolic solution initially containing Cr(III) and H_2CA in an exactly 2:1 mole ratio clearly confirmed the existence of such a $Cr_2(CA_r)^{2+}$ species (see Experimental Section).

A yellow-green product with visible absorption peak positions and relative intensities quite similar to those of I and IV was obtained from the anaerobic, stoichiometric reduction of H_2CA by Cr^{2+}(aq) in 0.1 M $HClO_4$, confirming the earlier report.[8] All visible peaks (425, 454, 489, 592, 644 nm) are slightly blue-shifted relative to those of the CA_r complexes generated in ethanol. The remarkable similarity between these spectra and that of the chloranilate semiquinone trianion radical in 6 M NaOH (Figure 1B; λ_{max} 422, 447, 476 nm) should also be noted. Unlike I and IV in ethanol, the chromous-generated $Cr_2(CA_r)^{2+}$ product in 0.1 M $HClO_4$ is highly susceptible to aerobic oxidation. Thus, the visible absorption features of this complex disappeared within several hours after exposing a sample to air and were replaced by the 330- and 501-nm bands characteristic of III. Isosbestic points at 358, 514, and 588 nm pertained throughout this aerobic decay. The identity of the chromium products was established through chromatography of a partially oxidized sample. In order of elution by 0.5 M $LiClO_4$–0.1 M $HClO_4$, well-separated purple (III), yellow-green (reactant), and blue-violet ($Cr(H_2O)_6^{3+}$) bands were isolated and identified from their UV–visible spectra. A minor golden-brown fraction ($[(H_2O)_5Cr]_2O^{4+}$)[19] was eluted after $Cr(H_2O)_6^{3+}$, accounting for a pronounced 440-nm shoulder in the Cr^{2+}(aq)–H_2CA product spectrum that has no equivalent in those of I, IV, and chloranilate semiquinone. As anticipated from our rate studies of $[(H_2O)_5Cr]_2O^{4+}$ acid hydrolysis,[20] decay of this 440-nm feature was substantially slower than that of the other major 400–500-nm bands.

Ethanolic IV treated with sufficient Br_2 to fully oxidize the chloranilate moiety was subjected to chromatography in order to determine whether binuclear complexes of the benzoquinone (CA_{ox}) could be isolated. The light olive green product mixture containing 0.57 mmol of Cr and 0.20 mmol of CA was diluted with water and applied to a 20 × 2.5 cm column. Upon elution with 0.5 M $LiClO_4$–0.01 M $HClO_4$, all of the chloranilate emerged as III; there was no evidence for the presence of a $Cr_2(CA_{ox})^{4+}$ species, which should elute well behind the $Cr(H_2O)_6^{3+}$ fraction.

Magnetic and Electrochemical Measurements. The paramagnetic gram-susceptibility of chromium in a 99% ethanolic solution of binuclear complex I was found to be $(1.17 \pm 0.03) \times 10^{-4}$ cgsu (298.2 K), corresponding to an effective magnetic moment of 3.81 ± 0.05 μ_B. The 100 K EPR spectrum of the solution used in the magnetic susceptibility measurement showed a single, 75 G wide resonance at $g = 1.97$. Both room temperature and 100 K EPR spectra of compound II (powder) showed very broad (450 G line width) signals at $g = 1.98$. The insolubility of II prevented its characterization in solution. We note, however, that the transient absorption spectrum of II in 0.1 M $HClO_4$ is similar to those of the other Cr–CA_r complexes, with sharp peaks at 497 and 460 nm. Acid catalysis rather than aerobic oxidation is responsible for the rapid decay of II in $HClO_4$ media, as decomposition was found to be complete within 1 min in anaerobic 1 M $HClO_4$. The decay products, characterized by ultraviolet features at 265 (sh), 276, 285, 327, and 340 (sh) nm, have not yet been identified.

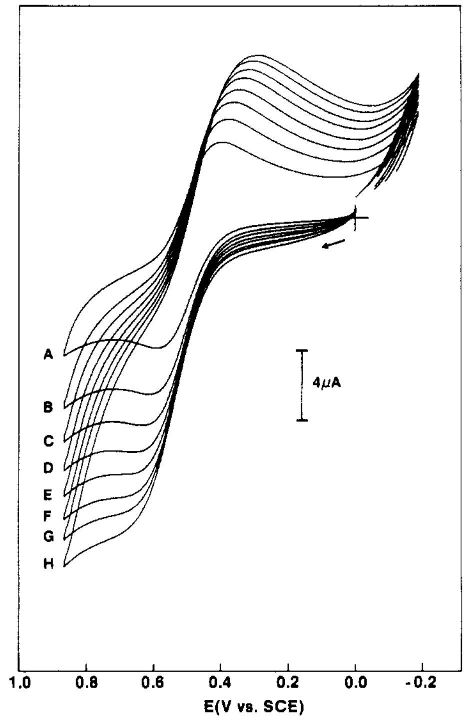

Figure 3. Cyclic voltammograms of 2.2 mM solutions of complex I in 99% ethanol (0.1 M $(n\text{-}C_4H_9)_4NClO_4$ supporting electrolyte, 25.0 °C, Pt-wire working and aqueous saturated calomel reference electrodes). Sweep rates (mV/s): A, 50; B, 100; C, 150; D, 200; E, 250; F, 300; G, 350; H, 400.

Cyclic voltammograms of 2.2 mM solutions of complex I were recorded at 25.0 °C in 99% ethanol (0.1 M $N(n\text{-}C_4H_9)_4ClO_4$ supporting electrolyte), aqueous 0.1 M NH_4ClO_4 (10% ethanol), and aqueous 0.1 M $HClO_4$ (10% ethanol). Samples examined were from the same stock solution used in the spectrophotometric, magnetic, and chromatographic studies. Quasi-reversible cyclic voltammograms were observed for I in 99% ethanol, within the range 50–400 mV/s (Figure 3). Large peak-to-peak separations were found, ranging from 197 (50 mV/s) to 315 mV (200 mV/s). No anodic peak was resolved at sweep rates faster than 200 mV/s. An apparent reduction potential of +0.49 V vs. SCE, independent of sweep rate, could be calculated as $(E_{pa} + E_{pc})/2$ from the 50, 100, 150, and 200 mV/s data. The i_{pa}/i_{pc} ratio at 50 mV/s, calculated by the method of Nicholson,[27] is 0.9 ± 0.1. Direct measurement of the anodic current base line was not possible, as another anodic process, presumably oxidation of Cr(III) to Cr(VI), ensues at applied potentials more positive than +0.8 V vs. SCE. A plot of i_{pa} vs. $v^{1/2}$ is linear, as expected for a reversible wave, but the intercept is not at zero current.

The calculation of $E°$ as $(E_{pa} + E_{pc})/2$ is highly questionable in view of the large sweep rate dependent peak-to-peak separations and apparent tendency of the I oxidation product to decompose into III and $Cr(H_2O)_6^{3+}$. An alternative analysis, based on eq 1 for a reversible wave,[28] involves only the anodic current–potential

$$E = E_{1/2} + (RT/nF) \ln [(i_d - i)/i] \qquad (1)$$

curve; $E_{1/2}$ and i_d represent the half-wave potential and diffusion current, respectively. With a freshly cleaned Pt working electrode, anodic linear-sweep voltammograms yielded excellent linear E vs. $\ln [(i_d - i)/i]$ plots with slopes of 32 ± 1 mV, in good agreement with that expected for a two-electron oxidation (30 mV), and intercepts ($E_{1/2}$) of 0.46 ± 0.01 V vs. SCE.

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Table II. Ethanol Oxidation Rate Constants[a]

[EtOH], M	[H_2O], M	[Cr(III)], mM	% EtOH (w/v)	temp, °C	$10^3 k_{obsd}$,[b] s^{-1}
16.94	0.41	16.0	99	60.0	1.48 (0.02)
16.77	0.91	16.0	98	60.0	1.26 (0.04)
16.59	1.42	16.0	97	60.0	1.05 (0.07)
16.42	1.91	16.0	96	60.0	0.70 (0.15)
16.26	2.41	16.0	95	60.0	0.49 (0.05)
16.06	3.33	16.0	94	60.0	0.34 (0.04)
15.80	4.17	16.0	92.5	60.0	0.19 (0.02)
16.94	0.41	0.100	99	60.0	0.37 (0.02)
16.94	0.41	0.401	99	60.0	0.50 (0.03)
16.94	0.41	0.802	99	60.0	0.49 (0.01)
16.94	0.41	2.00	99	60.0	0.53 (0.05)
16.94	0.41	2.52	99	60.0	1.05 (0.02)
16.94	0.41	3.01	99	60.0	1.46 (0.13)
16.94	0.41	4.01	99	60.0	1.40 (0.23)
16.94	0.41	8.02	99	60.0	1.50 (0.04)
16.94	0.41	32.0	99	60.0	1.50 (0.04)
16.94	0.41	16.0	99	19.1	0.010 (0.001)
16.94	0.41	16.0	99	30.0	0.039 (0.003)
16.94	0.41	16.0	99	40.9	0.41 (0.02)
16.94	0.41	16.0	99	49.5	1.11 (0.11)
16.94	0.41	16.0	99	70.4	2.34 (0.17)

[a] $[H_2CA]_0 = 0.04$ mM; N_2 atmosphere. [b] Average deviations from the mean shown in parentheses.

Neither anodic nor cathodic peaks were observed in cyclic voltammograms of I in 0.1 M $HClO_4$ (−0.2 to +0.8 V vs. SCE), indicative of highly irreversible behavior. Substantial anodic currents appeared in the same potential region as i_{pa} in 99% ethanol, but much smaller cathodic currents were found upon switching the scan direction. Broad anodic and cathodic maxima coupled with very large peak-to-peak separations (614 mV at 50 mV/s) characterized voltammograms of I in 0.1 M NH_4ClO_4 (carbon-paste or Pt working electrode). The ratio i_{pa}/i_{pc} was larger than the 99% ethanol value and slightly dependent upon sweep rate, varying from 1.20 (200 mV/s) to 1.36 (50 mV/s). The average of E_{pa} and E_{pc} obtained in 0.1 M NH_4ClO_4 (0.47 V vs. SCE; 50 mV/s) is in reasonable agreement with the 99% ethanol value.

Ethanol Oxidation Rate Studies. As was described briefly in the pioneering study,[8] the rate of chloranilic acid reduction by ethanol, catalyzed by chromic ion, is strongly dependent upon [Cr(III)], [ethanol], and temperature. The effects of all three of these variables on k_{obsd}, with H_2CA as the limiting reagent, are described in Table II. A rigorous quantitative fitting of these data to a rate law is not possible, as the effective dielectric constant of the medium necessarily varies with reductant concentration. Furthermore, constant ionic strength was not maintained in [Cr(III)] variation studies in order to avoid the competition between Cr(III) and another cation for chloranilate binding sites.

The [Cr(III)] variation results in 99% ethanol at 60 °C show that k_{obsd} increases rapidly within the interval 0.1–1.0 mM to a plateau at $5 \times 10^{-4}\ s^{-1}$. With further increases in chromic concentration, k_{obsd} again increases abruptly to a second plateau at $1.50 \times 10^{-3}\ s^{-1}$. The data may be understood in terms of the parallel oxidation of ethanol by 1:1 and 2:1 Cr(III)–CA_{ox} complexes, preceded by rapid complexation equilibria (eq 2). The

$$\mathrm{Cr(III)} + \mathrm{CA_{ox}}^{2-} \overset{K_1}{\rightleftharpoons} \mathrm{Cr(CA_{ox})^+}$$

$$\mathrm{Cr(III)} + \mathrm{Cr(CA_{ox})^+} \overset{K_2}{\rightleftharpoons} \mathrm{Cr_2(CA_{ox})^{4+}}$$

$$\mathrm{Cr(CA_{ox})^+} + \mathrm{C_2H_5OH} \xrightarrow{k_1} \mathrm{Cr(CA_r)^-} + \mathrm{CH_3CHO} + 2\mathrm{H^+} \qquad (2)$$

$$\mathrm{Cr(III)} + \mathrm{Cr(CA_r)^-} \xrightarrow{\text{fast}} \mathrm{Cr_2(CA_r)^{2+}}$$

$$\mathrm{Cr_2(CA_{ox})^{4+}} + \mathrm{C_2H_5OH} \xrightarrow{k_2} \mathrm{Cr_2(CA_r)^{2+}} + \mathrm{CH_3CHO} + 2\mathrm{H^+}$$

rate law implied by this mechanism, assuming that $[CA_{ox}]_{tot}$ = ($[Cr(CA_{ox})^+] + [Cr_2(CA_{ox})^{4+}]$), is given in eq 3. On this basis,

$$k_{obsd} = \frac{(k_1 + k_2K_2[\mathrm{Cr(III)}])[\mathrm{C_2H_5OH}]}{1 + K_2[\mathrm{Cr(III)}]} \qquad (3)$$

the rate constants corresponding to the first and second plateaus would be $k_1[C_2H_5OH]$ and $k_2[C_2H_5OH]$, respectively, and an upper limit of $1 \times 10^4\ M^{-1}$ may be placed on K_2.

In another set of 60 °C runs, the ethanol concentration dependence was evaluated in the range 90–100%; very small, slow 493-nm absorbance changes were seen at lower concentrations. The Cr(III) concentration was fixed at 1.60×10^{-2} M, within the second plateau region, such that k_{obsd} should be a function of k_2 and [EtOH] only at constant temperature. The rate of ethanol oxidation rises sharply above the 90% (15.4 M) level and varies with [EtOH] as described by eq 4 in the 95–99% range (a =

$$k_{obsd} = a + b[\mathrm{EtOH}] \qquad (4)$$

$-0.0236\ s^{-1}$, $b = 1.48 \times 10^{-3}\ M^{-1}\ s^{-1}$). Accordingly, the intercept must be subtracted from k_{obsd} in order to calculate k_2 from eq 3. The k_2 value calculated by this method, $(1.5 \pm 0.1) \times 10^{-3}\ M^{-1}\ s^{-1}$, is in excellent agreement with the slope of the k_{obsd}–[EtOH] correlation.

Finally, our results confirm the reported[8] large temperature coefficient of the chromic ion catalyzed EtOH–H_2CA reaction. The linearity of an Arrhenius plot based on the results in Table II is only fair, giving an apparent E_a of 22 ± 3 kcal/mol in 99% EtOH.

Discussion

The room-temperature spectrophotometric titration results clearly show that a 2:1 Cr:CA_{ox} mole ratio is required for the catalyzed oxidation of ethanol, as no reduction of chloranilate was observed within the 1:1 complex III. However, the 60 °C kinetic results suggest that the catalytic reactivities of 1:1 and 2:1 Cr–CA_{ox} complexes become comparable at elevated temperatures. While 2:1 Cr–CA_r species were identified by chromatography (I) and in the Cr^{2+}(aq)–H_2CA reaction, a 5:2 Cr:CA_r ratio evidently pertains for the thermodynamic catalyst reduction product in the presence of excess Cr(III). The favorability of this stoichiometry is further supported by the elemental analysis of II.

The rich UV–visible spectra of I, III, and IV merit a careful analysis, as all are dominated by intense, sharp peaks that clearly cannot be d–d transitions arising from the d^3 electronic configuration of Cr(III). Although the point group of the chloranilate dianion is only C_{2h}, spectra of substituted 1,4-benzoquinones may be conveniently interpreted by comparison with the parent molecule (D_{2h}).[29-31] The π-electronic configuration of 1,4-benzoquinones, in order of increasing LCAO–MO energy, is $(b_{1u})^2(b_{2g})^2(b_{1u})^2(b_{3g})^2(b_{2g})^0(a_u)^0(b_{1u})^0(b_{2g})^0$.[29] On this basis, both symmetry-allowed b_{1u}–b_{2g} (LUMO) ($^1B_{3u} \leftarrow {}^1A_g$) and symmetry-forbidden b_{3g}–b_{2g} ($^1B_{1g} \leftarrow {}^1A_g$) π–π^* transitions are expected, along with an n–π^* band at lower energy.[29] The π–π^* and n–π^* transitions are red- and blue-shifted, respectively, by electron-donating substituents.[30,31] With reference to the spectrum of 1,4-benzoquinone,[29-31] we assign the 330- and 501-nm bands of III as $^1B_{3u} \leftarrow {}^1A_g$ and $^1B_{1g} \leftarrow {}^1A_g$ (overlapping n–π^*), respectively. The symmetry forbiddenness of the latter transition is relaxed somewhat by unsymmetrical substitution of the quinonoid ring.[29,30] Thus, the 520-nm extinction coefficient of HCA^- in water ($9.14 \times 10^2\ M^{-1}\ cm^{-1}$) is substantially larger than those of both H_2CA ($1.41 \times 10^2\ M^{-1}\ cm^{-1}$) and CA^{2-} ($1.74 \times 10^2\ M^{-1}\ cm^{-1}$) (25 °C, I = 0.5 M).[11] The intensity of the $Cr(CA_{ox})^+$ 501-nm band therefore is consistent with a structure involving the interaction of Cr(III) with only one of the available phenolic oxygen atoms of the quinone.

A striking similarity exists among the visible spectra of I, II, IV, and the chloranilate semiquinone trianion radical ($CASQ^{3-}$). Indeed, analogous patterns, composed of two intense, sharp peaks accompanied (in some cases) by a high-energy shoulder, have been

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reported for many fully ionized 1,4-benzosemiquinones in the 400–500-nm region.[32-35] We will refer to these 400–500-nm features as bands A, B, and C, in order of increasing energy. Although transition energies vary modestly throughout the series, the energy differences between bands, ΔE_{AB} and ΔE_{BC}, are nearly invariant in the comparison of $CASQ^{3-}$ ($\Delta E_{AB} = 1.4 \times 10^3$ cm^{-1}, $\Delta E_{BC} = 1.3 \times 10^3$ cm^{-1}) with IV ($\Delta E_{AB} = \Delta E_{BC} = 1.6 \times 10^3$ cm^{-1}) and the product of the Cr^{2+}(aq)–H_2CA reaction ($\Delta E_{AB} = \Delta E_{BC} = 1.5 \times 10^3$ cm^{-1}). These relationships confirm the analogy among the three spectra and imply that Cr perturbs the electronic structure of $CASQ^{3-}$ through an interaction with a donor or acceptor molecular orbital involved in all three essentially ligand-centered electronic transitions. Surprisingly, no detailed assignment of 1,4-benzosemiquinone spectra is available in the literature, even though these visible bands have been utilized to obtain ionization constants and disproportionation rates.[32]

An extensive literature in the area of stable transition-metal–1,2-semiquinone complexes has developed in the last 10 years, including several structural and spectroscopic studies of chromium(III) compounds with such ligands as 3,5-di-*tert*-butyl-1,2-benzosemiquinone (3,5-DTBSQ) and tetrachloro-1,2-benzosemiquinone (TCSQ).[5,36-39] Visible spectra of these Cr(III)–semiquinone adducts invariably exhibit intense bands near 500 nm analogous to those reported here, although with poorer resolution of proximal features.[36,37] Strong antiferromagnetic coupling between transition-metal d electrons and semiquinone unpaired electrons has been proposed to account for the magnetic susceptibilities and EPR spectra of Cr(III) complexes with various combinations of quinone, semiquinone, and catecholate ligands.[5] Thus, the coupling of a Cr(III) $S = {}^3/_2$ center with three $S = {}^1/_2$ semiquinone ligands would account for the diamagnetism of $Cr(3,5\text{-DTBSQ})_3$ and weak paramagnetism of $Cr(TCSQ)_3$ at room temperature.[40]

The two-electron-reduction product of $Cr_2(CA_{ox})^{4+}$ would contain three unpaired electrons per chromium atom if Cr(III)–bridging chloranilate hydroquinone–Cr(III) were the predominant resonance form (with weak antiferromagnetic coupling between Cr centers). In contrast, four unpaired electrons per chromium atom would pertain if Cr(II) (high-spin)–CASQ–Cr(III) defines the electronic structure. The 298.2 K μ_{eff}/Cr of 3.81 μ_B characteristic of I is slightly less than the $S = {}^3/_2$ spin-only value (3.87 μ_B), as is typical (eq 5; λ is the many-electron spin–

$$\mu_{eff} = 2(1 - 4\lambda/10Dq)[S(S + 1)]^{1/2} \qquad (5)$$

orbit coupling constant) of octahedral Cr(III) complexes.[41] The g value of 1.97 implied by μ_{eff} is in exact agreement with the 100 K EPR result. Factors that may contribute to the unusually large EPR line width[42] include spin–spin interactions among the paramagnetic centers and intramolecular electron exchange within I. The magnetic susceptibility and visible spectral results could be reconciled by invoking strong antiferromagnetic exchange between $S = 2$ Cr(II) and $S = {}^1/_2$ bridging-semiquinone centers, supported by $d\pi(t_{2g})$–$\pi^*(b_{2g}(\text{HOMO}))$ orbital overlap. While a low-spin Cr(II) center would not result from a six-oxygen (H_2O, EtOH, phenolate) ligand field, molecular orbital theory[43] provides an attractive alternative to magnetic exchange in the understanding of both magnetic and spectroscopic properties of I.

Only a qualitative molecular orbital analysis of binuclear Cr(III)–$CASQ^{3-}$ complexes may be offered in view of the limited structural information available. Nevertheless, an essentially planar $Cr_2(CA_r)^{2+}$ structure involving 1,2 and 4,5 chelating pairs of oxygen atoms[8] appears reasonable in light of X-ray crystallographic findings on chloranilate-bridged Ni(II) and Cu(II) binuclear compounds.[16] From the molecular orbital analysis of Pierpont et al.,[16] these planar (xy) units are assumed to have D_{2h} symmetry, with the Cr–Cr vector defining the x axis. Considering only π bonding, the Cr $t_{2g}(O_h)$ orbitals generate b_{1u} ($xz(1) + xz(2)$), b_{2g} ($xz(1) - xz(2)$), b_{3g} ($yz(1) + yz(2)$), a_u ($yz(1) - yz(2)$), b_{2u} ($xy(1) + xy(2)$), and b_{1g} ($xy(1) - xy(2)$) symmetry orbitals. Of these, b_{1g} and b_{2u} are rigorously nonbonding with respect to the semiquinone π system. The calculations of Gordon and Fenske show that the Cr(III) 3d valence orbitals fall only about 1 eV lower in energy than the $3b_1$ (C_{2v}) semiquinone HOMO in the complexes $[Cr(BQ)_{3-n}(SQ)_n]^{(3-n)+}$ (n = 1, 2, 3), where BQ and SQ represent 1,2-benzoquinone and semiquinones, respectively.[43] On this basis, substantial bonding energies were predicted for molecular orbitals derived from Cr(3d)–$3b_1$(SQ) overlaps.[43] Similarly, we anticipate that a bonding, primarily metal-localized $2b_{2g}$ molecular orbital will result from the interaction between the $CASQ^{3-}$ HOMO and Cr b_{2g} symmetry orbitals. The corresponding ligand-centered antibonding level ($3b_{2g}$) would then be destabilized relative to the HOMO of free $CASQ^{3-}$. The Cr b_{1u}, b_{3g}, and a_u orbitals are expected to be approximately nonbonding, as symmetry-allowed overlaps would be with $CASQ^{3-}$ levels at much higher or lower energy than the HOMO.[30]

Including the four strongly bonding ligand levels, 16 electrons must be accommodated in the $Cr_2(CA_r)^{2+}$ π system. A reasonable electronic configuration of I consistent with both magnetic and spectroscopic findings is $(1b_{1u})^2(1b_{2g})^2(2b_{1u})^2(1b_{3g})^2(2b_{2g})^2(1a_u)^1(1b_{1g})^1(1b_{2u})^1(3b_{1u})^1(2b_{3g})^1(3b_{2g})^1(2a_u)^0(4b_{1u})^0(4b_{2g})^0$, provided that the energy difference between the ligand-centered HOMO and nonbonding $1a_u$, $1b_{1g}$, $1b_{2u}$, $3b_{1u}$, and $2b_{3g}$ orbitals localized on Cr is, in fact, small. This molecular orbital approach accounts for three unpaired electrons per chromium atom through the pairing of two electrons in the bonding $2b_{2g}$ MO, delocalized over both Cr atoms.

A qualitative MO analysis also provides a reasonable basis for understanding some aspects of the electronic spectra of I, II, and IV. We assign the intense $CASQ^{3-}$ bands at 476 and 447 nm to excitations from the b_{2g} HOMO to the LUMO a_u (${}^2A_u \leftarrow {}^2B_{2g}$) and b_{1u} (${}^2B_{1u} \leftarrow {}^2B_{2g}$) antibonding levels. Red shifts in the analogous transitions of $Cr_2(CA_r)^{2+}$ complexes are expected from the destabilization of the $3b_{2g}$ HOMO associated with Cr–$CASQ^{3-}$ π bonding. Destabilization of the $3b_{2g}$ MO would move the $2b_{1u}$–$3b_{2g}$ and $1b_{3g}$–$3b_{2g}$ transitions to higher energy, as compared with the analogous bands in both $CASQ^{3-}$ and CA^{2-}. The 300-nm absorption of I and IV therefore should contain the former π–π^* transition along with a phenolate oxygen-to-chromium charge-transfer component.[19] Considering the apparent energetic proximity of $3b_{2g}$ and Cr-centered nonbonding orbitals, the comparatively broad, asymmetric complex I (and IV) band with λ_{max} at 355 nm may contain several transitions of the metal (3d)-to-ligand (π^*) charge-transfer type, i.e. $1b_{1g}$–$2a_{2u}$. Such bands have been observed (360–400 nm) in nickel(0) complexes of duroquinone.[44] Finally, we note that the 600 (ϵ/Cr 2.4×10^2 M^{-1} cm^{-1}) and 654 nm (ϵ/Cr 4.8×10^2 M^{-1} cm^{-1}) complex I (and IV) bands, which have no analogues in the $CASQ^{3-}$ spectrum, arise from the splitting of the ${}^4T_{2g} \leftarrow {}^4A_{2g}(O_h)$ Cr(III) d–d transition by a low-symmetry (presumably C_{2v}) crystal field component. A crystal field analysis of similar splitting in the spectrum of $[(H_2O)_5Cr]_2O^{4+}$ has been reported.[20]

Several lines of evidence point to low thermodynamic and kinetic stability of the immediate $Cr_2(CA_r)^{2+}$ oxidation product, $Cr_2(CA_{ox})^{4+}$. No chloranilate-containing 4+ cation was found in the

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chromatographic separation of product mixtures from the oxidations of IV by Br_2 in ethanol and of $Cr_2(CA_r)^{2+}$ by O_2 in water. Isosbestic points observed throughout the latter reaction confirm the absence of significant concentrations of products other than $Cr(H_2O)_6^{3+}$ and $Cr(CA_{ox})^+$. The grossly irreversible cyclic voltammograms of $Cr_2(CA_r)^{2+}$ in 0.1 M NH_4ClO_4 and 0.1 M $HClO_4$, with $i_{pa}/i_{pc} > 1$, suggest that the anodic oxidation rate and aqueous stability of $Cr_2(CA_{ox})^{4+}$ both fall off rapidly with increasing $[H^+]$.

The $Cr_2(CA_{ox})^{4+}$ species evidently is somewhat less susceptible to decay in 99% ethanol, as indicated by quasi-reversible voltammograms with i_{pa}/i_{pc} near 1. Nevertheless, peak-to-peak separations consistently were much larger than the value of 30 mV characteristic of a reversible, two-electron process. The 60 °C kinetic results demonstrate that a 100-fold excess of Cr(III) over H_2CA is needed to fully convert chloranilate into $Cr_2(CA_{ox})^{4+}$, even in 99% ethanol. The oxidizing strength of the quinonoid moity in $Cr_2(CA_{ox})^{4+}$ is strongly enhanced relative to that of free H_2CA in ethanol. Thus, the apparent $Cr_2(CA_{ox})^{4+}/Cr(CA_r)^{2+}$ $E_{1/2}$ of 0.46 V vs. SCE may be compared with that of 0.42 V vs. NHE (EtOH) reported for H_2CA in 95% EtOH–1 M HCl.[12] On this basis, we estimate a $\Delta E_{1/2}(Cr_2(CA_{ox})^{4+}$ vs. $H_2CA)$ of +0.28 V, corresponding to a substantial increase in the thermodynamic driving force (13 kcal/mol in $\Delta G°$).

The capability of $Cr_2(CA_{ox})^{4+}$, but not H_2CA, as an ethanol oxidation catalyst is a likely consequence of this increase in the thermodynamic driving force. Oxidation of primary alcohols typically proceeds through hydride ion transfer to the two-electron acceptor.[1] The first-order C_2H_5OH dependence observed above 16 M is consistent with rate-limiting direct hydride ion transfer from C_2H_5OH to the bridging CA_{ox}^{2-} ligand. A change of order from first to zeroth or simple zeroth-order ethanol dependence would be expected for the rate-determining two-electron transfer from coordinated C_2H_5OH to CA_{ox}^{2-}, mediated by the Cr atom. As was noted in the pioneering study,[8] the zeroth-order limiting [Cr(III)] dependence in 99% ethanol implies that substitution in the first coordination sphere of Cr(III), to form $Cr_2(CA_{ox})^{4+}$ from the separated reactants, is fast on the time scale of the redox process. The much slower rate of Cr(III) ligand substitution documented for predominantly aqueous solutions[45] accounts for the failure of chromic ion to catalyze the C_2H_5OH–H_2CA redox reaction in <90% ethanol.

The isolation of a solid containing the $Cr_2(CA_r)^{2+}$ unit was only partially successful, as II could not be redissolved in ethanol to give I or IV. Nevertheless, the transient visible spectrum in 0.1 M $HClO_4$ and the powder EPR signal are quite similar to those of the other $Cr-CASQ^{3-}$ complexes. Compound II evidently is a complex salt containing sodium and chromium cations to balance perchlorate, hydroxide, and chloranilate semiquinone anions. Charges balance to give a formula in good agreement with elemental analyses if chromium and chloranilate are present exclusively as Cr(III) and $CASQ^{3-}$, respectively, giving a neutral $Cr_5(CASQ)_2(ClO_4)_9$ core. The 13 Na^+ cations present per $Cr_5(CASQ)_2^{9+}$ unit presumably offset the charges of hydroxo ligands. Since II could not be recrystallized, we cannot be certain that the compound is entirely homogeneous, particularly with respect to Na^+, OH^-, and H_2O content. Nevertheless, the Cr, C, and Cl analyses strongly support the proposed 5:2 Cr(III):$CASQ^{3-}$ stoichiometry. The infrared spectrum of II is not particularly informative but does show a decrease in the C=O stretching frequency (1525 cm^{-1}) and band intensity compared with those of $Na_2CA \cdot 2H_2O$ (1560 cm^{-1}), as would be expected for a semiquinone complex. Although the structure of II remains in doubt, a particularly intriguing possibility, currently under investigation, involves the interaction of two parallel, planar $Cr_2(CASQ)^{3+}$ units, as ligands, with a central Cr(III) ion to form a π "sandwich" complex similar to bis(duroquinone)nickel(0).[44]

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Registry No. H_2CA, 87-88-7; Cr, 7440-47-3; ethanol, 64-17-5.

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Synthesis and Characterization of ((Trimethylsilyl)amino)- and (Methyl(trimethylsilyl)amino)gallium Dichloride

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The reaction of $GaCl_3$ with $(Me_3Si)_2NH$ has been found to yield $[Cl_2GaN(H)SiMe_3]_2$, and $[Cl_2GaN(Me)SiMe_3]_2$ was obtained from the reaction of $GaCl_3$ with $(Me_3Si)_2NMe$. The trans isomer of each dimer was identified in the solid state from X-ray crystallographic studies. Crystal data for *trans*-$[Cl_2GaN(H)SiMe_3]_2$: orthorhombic space group *Pbca* (No. 61), $a = 9.207$ (2) Å, $b = 18.331$ (5) Å, $c = 11.344$ (2) Å, $V = 1914.6$ (8) Å^3, $Z = 4$, ρ(calcd) = 1.588 g cm^{-1}. Crystal data for *trans*-$[Cl_2GaN(Me)SiMe_3]_2$: monoclinic space group $P2_1/c$ (No. 14), $a = 11.594$ (5) Å, $b = 13.024$ (7) Å, $c = 13.663$ (5) Å, $\beta = 91.38$ (4)°, $V = 2062$ (2) Å^3, $Z = 4$, ρ(calcd) = 1.564 g cm^{-1}. NMR data indicate the existence of an equilibrium mixture of $[Cl_2GaN(H)SiMe_3]_3$, *trans*-$[Cl_2GaN(H)SiMe_3]_2$, and *cis*-$[Cl_2GaN(H)SiMe_3]_2$ in solutions of ((trimethylsilyl)amino)gallium dichloride and an equilibrium mixture of the cis and trans isomers in solutions of $[Cl_2GaN(Me)SiMe_3]_2$. The temperature and solvent dependences of the equilibria were examined by ^1H NMR spectroscopy. The results of this study and the ^{13}C and ^{29}Si NMR spectra in toluene are reported.

Introduction

Reactions involving the cleavage of a Si–N bond in bis(trimethylsilyl)amine and substituted (trimethylsilyl)amines by gallium trichloride and alkylgallium dichlorides have been found to readily yield (substituted amino)gallium dichlorides and alkyl(amino)gallium chlorides. Substituted (trifluoroacetanilido)gallium dichlorides have been prepared from reactions of gallium trichloride with the corresponding substituted (trimethylsilyl)amines,[2] and ((trimethylsilyl)amino)gallium dichloride has been isolated from the thermal decomposition of (bis(tri-

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[2] Meller, A.; Maringgele, W.; Oesterle, R. *Monatsh. Chem.* **1980**, *111*, 1087.