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Oxidation of Alcohols, Aldehydes, and Carboxylates by the Aquachromium(IV) Ion

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Abstract: Four methods have been developed to prepare aquachromium(IV), which we believe to be an oxo ion, CrO^{2+}. It readily converts Ph_3P to Ph_3PO ($k = 2.1 \times 10^3$ L mol^{-1} s^{-1}) at 25 °C in 85% CH_3CN/H_2O (0.10 M $HClO_4$). The reactions used to form CrO^{2+} are those between Cr^{2+} and (a) O_2 (b) anaerobic CrO_2^{2+}, (c) anaerobic $CrOOCr^{4+}$, and (d) anaerobic Tl(III). The CrO^{2+} has a half-life of 30 s in acidic solution at room temperature and will oxidize alcohols, aldehydes, and certain carboxylates as well as diethyl ether. The second-order rate constants (L mol^{-1} s^{-1}) in acidic solution (μ = 1.0 M $HClO_4/LiClO_4$, 25 °C) are as follows: CH_3OH, 52; CD_3OH, 15; C_2H_5OH, 88; C_2D_5OH, 41; $(CH_3)_2CHOH$, 12.0; $(CD_3)_2CDOH$, 4.6; $CH_2{=}CHCH_2OH$, 101; $CH_3(CH_2)_2CH_2OH$, 44; $(C_2H_5)(CH_3)CHOH$, 41; $(CH_3)_3CCH_2OH$, 39; $C_6H_5CH_2OH$, 56; $(C_6H_5)(CH_3)CHOH$, 30; $(C_6H_5)_2CHOH$, 10.5; p-$CH_3OC_6H_4CH_2OH$, 71; p-$CH_3C_6H_4CH_2OH$, 66; p-$CF_3C_6H_4CH_2OH$, 60; c-C_4H_7OH, 44; c-C_5H_9OH, 31; $HCHO{\cdot}H_2O$, 92; $(CH_3)_3CCHO$, 37; HCO_2H, 11.6; HCO_2^-, 6.9×10^3; $HC_2O_4^-$, 2.2×10^3; $(C_2H_5)_2O$, 4.5. Activation parameters were also determined for selected reactions. In all but two of these reactions (cyclobutanol and pivaldehyde), Cr^{2+} is the immediate product as shown by trapping with O_2. On the basis of the kinetic and product data, the mechanism of oxidation by CrO^{2+} is proposed to be hydride transfer. The reactivity order for alcohols (1° > CH_3 > 2°), the small substituent effect for the benzyl alcohols, and the similarity of all the rate constants regardless of the organic substrate are inconsistent with the formation of carbon-centered radicals. The reaction of $HCrO_4^-$ with $(CH_3)_2CHOH$ is also shown to involve CrO^{2+} and Cr^{2+} as intermediates. The latter reacts with $HCrO_4^-$ with a rate constant of 2×10^9 L mol^{-1} s^{-1} in 2.0 M $HClO_4$.

Introduction

The intermediate IV and V oxidation states of chromium proved elusive to coordination chemists for many years. Recently, complexes of Cr(V) with Schiff base[1] and carboxylate ligands[2] have been isolated in which the V oxidation state is stable enough to permit spectroscopic and even crystallographic characterization. The IV oxidation state is known as a diperoxo species[3] and with the tetraphenylporphyrin ligand.[4] Recently, electrochemical and kinetic evidence for a Cr(IV) intermediate was obtained in the reduction of bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) by one-electron reducing agents[5a] and reduction of $HCrO_4^-$ by two-electron reducing agents, such as As(III), in the presence of the 2-ethyl-2-hydroxybutanoate ligand.[5b] Without such ligand stabilization, i.e., as an aqua complex, Cr(IV) has generally been considered unstable and highly reactive.[6] We present evidence to the contrary in this report.

It has long been recognized that the one- and two-electron oxidations of various metal ions[7] and organic substrates[8] by H_2CrO_4 must proceed through hydrated Cr(IV) and -(V) species. Evidence has been presented[9] for the intermediacy of Cr(V) in the oxidation of alcohols and carboxylates by H_2CrO_4, where the electron spin resonance (ESR) signal of a tetragonally distorted d^1 species can be attributed to Cr(V). This Cr(V) species almost certainly contains coordinated alcoholate or carboxylate ligands. Hydrated Cr(IV) has not been observed directly, even though it has been invoked in many mechanisms[10] as a transient which reacts rapidly with other species in the reaction mixture. Also, the reaction of $Cr(H_2O)_6^{3+}$ with strong oxidants[11] involves these same intemediates.

In this work, we describe the preparation of aqueous Cr(IV) in the absence of stabilizing ligands. This species was discovered during an investigation of the catalytic reactions of the superoxochromium(III) ion, CrO_2^{2+}.[12] (Throughout this work, coordinated water molecules are not shown.) Cr(IV) reacts with Ph_3P with a rate constant of $(2.1 \pm 0.2) \times 10^3$ M^{-1} s^{-1} in 85% CH_3CN/H_2O (0.10 M $HClO_4$) at 25 °C to give Ph_3PO and Cr^{2+}, which is trapped by O_2 to become CrO_2^{2+}. On this basis, and by analogy with the known $Cr^{IV}{=}O$ unit in porphyrin chemistry,[4] we have assigned to Cr(IV)$_{aq}$ the formula CrO^{2+}. We present evidence that this Cr(IV) species is the same as the proposed intermediate in the reaction of H_2CrO_4 with alcohols. The CrO^{2+} is stable enough (half-life 30 s in 1 M $HClO_4$) to use as a bulk reagent in mechanistic studies. The kinetics of the reactions of CrO^{2+} with various alcohols, aldehydes, and carboxylates are described, and a hydride-transfer mechanism common to all these reactions is proposed. Although much of the literature on Cr(IV) reactions is based on the assumption that Cr(IV) is exclusively a one-electron oxidant,[13,14] we show that this is rarely the case. For reactions with organic substrates, a two-electron path is not only thermodynamically viable but unequivocally observed.

$$CrO^{2+} + RH_2 \rightarrow Cr^{2+} + R + H_2O \tag{1}$$

Experimental Section

CrO^{2+} was usually prepared by syringe-injection of an air-free solution of Cr^{2+} (from Zn/Hg reduction of $Cr(H_2O)_6^{3+}$) into an acidic aqueous solution containing O_2. At very low Cr^{2+}:O_2 ratios, ca. 0.05:1, the adduct

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CrO_2^{2+} is formed quantitatively.[15] The CrO_2^{2+} was identified and quantified by its intense and characteristic UV spectrum: $\epsilon_{290nm} = 3100$ M^{-1} cm^{-1}, $\epsilon_{245nm} = 7000$ M^{-1} cm^{-1}.[16] At higher Cr^{2+}:O_2 ratios, for example 1:1, with efficient mixing in a stopped-flow jet, the CrO^{2+} is formed in ca. 30% yield (other products are nonoxidizing, low-absorbing Cr(III) species). At intermediate ratios, a mixture of CrO^{2+} and CrO_2^{2+} is produced. The superoxo complex CrO_2^{2+} is stable for at least half an hour at room temperature under O_2, and on this time scale does not react with any of the organic substrates studied here. In experiments where the product of the CrO^{2+} reaction is Cr^{2+}, it was necessary to work in the intermediate concentration regime (0.15 Cr^{2+}/O_2). Under these conditions, the Cr^{2+} product is trapped efficiently by oxygen, thus avoiding the autocatalytic consumption of CrO_2^{2+} by Cr^{2+}, eqs 1 and 2.[12]

$$CrO_2^{2+} + 2Cr^{2+} + H_2O \rightarrow CrO^{2+} + Cr(OH)_2Cr^{4+} \quad (2)$$

Reactions of CrO^{2+} were monitored in three ways. Occasionally, the absorption of CrO^{2+} itself (λ 260 nm, $\epsilon = (5 \pm 1) \times 10^3$ M^{-1} cm^{-1}, see below) was used. Many reactions were conducted in O_2-saturated solutions. In these cases, the product Cr^{2+} (eq 1) was rapidly converted to CrO_2^{2+}, which was monitored at 290 or 240 nm. Some reactions were conducted by adding $ABTS^{2-}$ (2,2′-azinobis(3-ethylbenzthiazoline-6-sulfonate)) simultaneously with the organic substrate. The formation of $ABTS^{\bullet-}$ (λ 417 nm, $\epsilon = 3.47 \times 10^4$ M^{-1} cm^{-1}; λ 645 nm, $\epsilon = 1.35 \times 10^4$ M^{-1} cm^{-1})[17] concurrent with substrate oxidation provided a convenient kinetic probe. Rate constants from the three methods agreed.

In a typical experiment, 0.2 mM Cr^{2+} was injected into O_2-saturated acidic solution (pH maintained by $HClO_4$, ionic strength by $LiClO_4$) containing at least a 10-fold excess of the appropriate organic substrate. Results were identical when the organic substrate was added after the Cr^{2+}, or when equal volumes of 0.2 mM Cr^{2+} and 1.26 mM O_2 solutions containing the organic substrate were mixed in a Durrum stopped-flow spectrophotometer. The absorbance changes due to buildup of CrO_2^{2+} as CrO^{2+} reacted with the substrate were monitored either at the 290 or 245 nm maximum of CrO_2^{2+}. Temperature was controlled at 25.0 ± 0.2 °C by means of a thermostated cell-holder connected to a circulating water bath. All data were fit to a pseudo-first-order equation, since the rate of CrO_2^{2+} formation from the rapid[16] reaction between Cr^{2+} and O_2 is governed by the rate of reaction 1. Thus $d[CrO_2^{2+}]/dt = k_1[CrO^{2+}][RH_2]$, and with $[RH_2]_0 \gg [CrO^{2+}]_0$, first-order kinetics are obeyed.

In contrast, the kinetic data in the presence of $ABTS^{2-}$ fit a biexponential rate law, since $ABTS^{2-}$ reacts with both CrO_2^{2+} and CrO^{2+} to form the intensely-colored radical anion $ABTS^{\bullet-}$. The CrO_2^{2+} is inevitably formed in experiments with all but the highest Cr^{2+}:O_2 ratios. That is, reactions 3 and 4 occur simultaneously, such that the buildup of $ABTS^{\bullet-}$ follows the rate law given in eq 5. Data were analyzed to

$$CrO^{2+} + ABTS^{2-} + H^+ \rightarrow CrOH^{2+} + ABTS^{\bullet-} \quad (3)$$

$$CrO_2^{2+} + ABTS^{2-} + H^+ \rightarrow CrO_2H^{2+} + ABTS^{\bullet-} \quad (4)$$

$$d[ABTS^{\bullet-}]/dt = k_3[ABTS^{2-}][CrO^{2+}] + k_4[ABTS^{2-}][CrO_2^{2+}] \quad (5)$$

determine k_3 and k_4, and the k_4 value agrees with that evaluated independently by mixing $ABTS^{2-}$ with a pure sample of CrO_2^{2+}. In the presence of substrate RH_2, the observed rate constant for the slower phase, $k_{slow} = k_4[ABTS^{2-}]$, is unchanged. The observed rate constant for the faster phase increases with $[RH_2]$ since CrO^{2+} is consumed in a parallel reaction with RH_2. Thus $k_{fast} = k_3[ABTS^{2-}] + k_1[RH_2]$.

In much of this work, CrO^{2+} was prepared by injection of Cr^{2+} into O_2-saturated aqueous $HClO_4$ (0.02–1.0 M), as described above. In some cases it was prepared by mixing of Cr^{2+} and O_2 solutions in the stopped-flow apparatus, with one of the solutions containing the desired organic substrate. As reported earlier,[18] CrO^{2+} is also made by three other reactions, eqs 2, 6, and 7, all anaerobic. As in the earlier work,

$$CrOOCr^{4+} + Cr^{2+} + H_2O \rightarrow CrO^{2+} + Cr(OH)_2Cr^{4+} \quad (6)$$

$$TlOH^{2+} + Cr^{2+} \rightarrow Tl^+ + CrO^{2+} + H^+ \quad (7)$$

enough experiments were done with these other sources of CrO^{2+} that we are confident the same oxochromium ion results from each, by virtue of identical reaction kinetics.

The ultraviolet spectrum of CrO^{2+} was obtained by mixing 0.26 mM O_2 and 0.3 mM Cr^{2+} in a Durrum stopped-flow apparatus equipped with a rapid-scan monochromator. Extinction coefficients were obtained by adding $ABTS^{2-}$ and measuring the amount of the intensely-colored radical anion $ABTS^{\bullet-}$ formed.

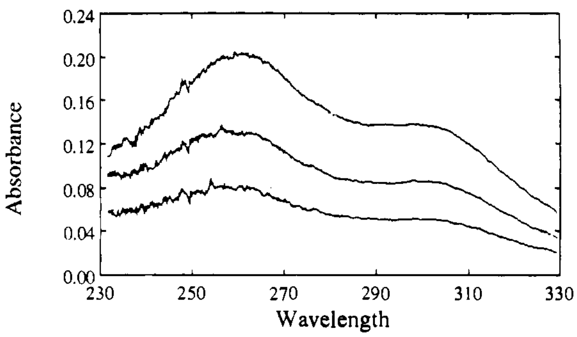

Figure 1. Difference spectra of CrO^{2+} formed by stopped-flow mixing of 0.3 mM Cr^{2+} and 0.26 mM O_2 in 1.0 M $HClO_4$. Time interval between spectra is 20 s. Spectra were obtained by difference from the spectrum at 60 s. The yield of CrO^{2+} is 15% based on total Cr. Path length was 2 cm.

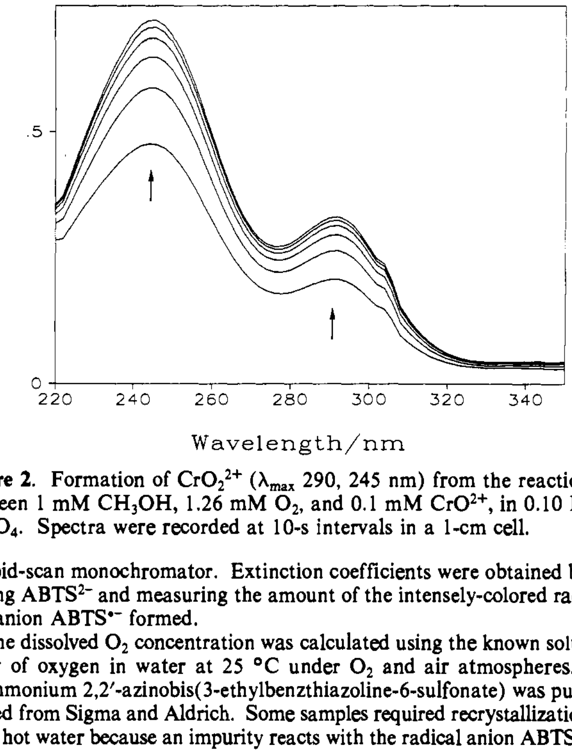

Figure 2. Formation of CrO_2^{2+} (λ_{max} 290, 245 nm) from the reaction between 1 mM CH_3OH, 1.26 mM O_2, and 0.1 mM CrO^{2+}, in 0.10 M $HClO_4$. Spectra were recorded at 10-s intervals in a 1-cm cell.

The dissolved O_2 concentration was calculated using the known solubility of oxygen in water at 25 °C under O_2 and air atmospheres.[19] Diammonium 2,2′-azinobis(3-ethylbenzthiazoline-6-sulfonate) was purchased from Sigma and Aldrich. Some samples required recrystallization from hot water because an impurity reacts with the radical anion $ABTS^{\bullet-}$ in the presence of a large concentration (mM) of $ABTS^{2-}$. Thallium(III) sulfate, CrO_3, $NaHCO_2$, $NaHC_2O_4$, and the various alcohols, aldehydes, and ethers were purchased from commercial sources and used as received. Solutions of HCHO were obtained by dissolving paraformaldehyde in warm 1 M $HClO_4$ and were standardized by chromotropic acid analysis.[20] $CrOOCr^{4+}$ was prepared by a literature method[21] and was standardized spectrophotometrically ($\epsilon_{634nm} = 404$ M^{-1} cm^{-1}). Organic products were determined on an HP 5730A gas chromatograph equipped with a VZ-10 column.

Unless stated otherwise, the kinetic data were determined at 25.0 °C and 1.0 M ionic strength ($HClO_4$ + $LiClO_4$).

Results

Formation of CrO^{2+}. The reaction of Cr^{2+} with O_2 produces CrO_2^{2+} quantitatively only in the presence of a large (≥20-fold) excess of O_2. When O_2 is not in large excess, another short-lived oxidizing Cr species is formed which decays to nonoxidizing Cr products. We identified this short-lived species as oxochromium(IV) or CrO^{2+}. The reactions cited in eqs 2, 6, and 7 also yield CrO^{2+}.

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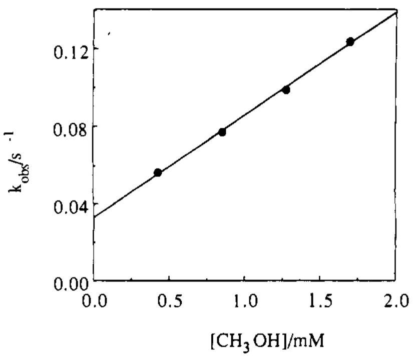

Figure 3. Dependence of the pseudo-first-order rate constants for the oxidation of CH_3OH by CrO^{2+} on the concentration of CH_3OH: 1.26 mM O_2, 0.10 M $HClO_4$, 0.90 M $LiClO_4$, 25.0 °C.

That the same species was produced in all three reactions was shown by conducting any one of the several reactions described subsequently with CrO^{2+} from an alternate source. This species is a fairly strong oxidant, as shown in subsequent work.

Spectrum of CrO^{2+}. Stopped-flow mixing of 0.3 mM Cr^{2+}_{aq} and 0.26 mM O_2 produces ~0.045 mM CrO^{2+}. The difference spectrum, shown in Figure 1 relative to the absorbance after CrO^{2+} has decomposed, has a peak at 260 nm ($\epsilon = (5 \pm 1) \times 10^3$ L mol^{-1} cm^{-1}) and a well-defined shoulder at 300 nm.

Reaction of CrO^{2+} with CH_3OH. The immediate addition of millimolar quantities of CH_3OH to O_2-saturated solutions containing 0.1 mM of CrO^{2+} causes the spectrum of CrO_2^{2+} to intensify, Figure 2.

The rate of formation of CrO_2^{2+} follows first-order kinetics, and the pseudo-first-order rate constants vary linearly with the concentration of CH_3OH at a given ionic strength, as shown in Figure 3. The plot has a nonzero intercept, 0.033 s^{-1} at $\mu = 1.0$ M, which appears repeatedly throughout this work and is not a characteristic of CH_3OH in particular. The slope of the plot gives $k_8 = 52.2 \pm 1.4$ L mol^{-1} s^{-1} as the rate constant for the reaction between CrO^{2+} and CH_3OH, eq 8, followed by eq 9. The rate

$$CrO^{2+} + CH_3OH \rightarrow Cr^{2+} + HCHO + H_2O \qquad (8)$$

$$Cr^{2+} + O_2 \rightarrow CrO_2^{2+} \qquad (9)$$

constant decreases to 15.1 ± 1.7 L mol^{-1} s^{-1} upon deuteration of the carbon-hydrogen bonds, eq 10, for an isotope effect $k_H/k_D = 3.46$. The rate constant for oxidation of CH_3OH is independent

$$CrO^{2+} + CD_3OH \rightarrow Cr^{2+} + DCDO + H_2O \qquad (10)$$

of $[O_2]$, provided O_2 is in excess, and of $[H^+]$ in the range 0.01-1.0 M, but decreases significantly with decreasing ionic strength. In H_2O at $\mu = 0.10$ M, the rate constant is $k_8 = 22.7 \pm 0.6$ L mol^{-1} s^{-1}. Rate constants were also determined for oxidation of CH_3OD in D_2O and CH_3OH in 6.3 M CH_3CN at 0.10 M ionic strength, with values of 23.8 ± 1.6 and 22.6 ± 1.6 L mol^{-1} s^{-1}, respectively.

HCHO was identified as the organic product by chromotropic acid analysis. Quantitation was difficult under kinetic conditions in the presence of O_2, because the inorganic product CrO_2^{2+} eventually oxidizes CH_3OH during its decomposition (by homolysis[15] to form Cr^{2+} followed by reactions 2 and 8, which form a catalytic cycle). CrO^{2+} is the only intermediate in the decomposition reaction which oxidizes CH_3OH on these time scales. The yield of HCHO was determined by analyzing an aged solution of pure CrO_2^{2+} to which CH_3OH was added. The yield of HCHO was found to be 430% based on the initial concentration of CrO_2^{2+}, implying induced oxidation of CH_3OH by O_2, eq 11.

$$O_2 + 2CH_3OH \xrightarrow{CrO_2^{2+}} 2HCHO + 2H_2O \qquad (11)$$

Since there is a large concentration excess of CH_3OH compared to $[CrO^{2+}]$, the ratio $[HCHO]/[CH_3OH]$ remains small under all kinetic conditions. The reactivity of HCHO toward CrO^{2+} has been determined independently (see below) and is comparable to that of CH_3OH. Therefore, CrO^{2+} reacts exclusively with CH_3OH under conditions where CH_3OH is present in excess, and we conclude that the only product is HCHO.

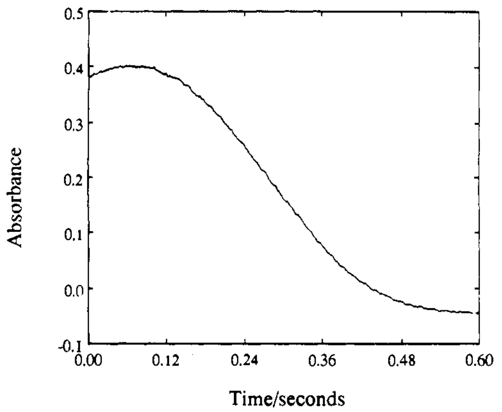

Figure 4. Kinetic trace showing the reaction of CrO^{2+} with 0.19 M CH_3OH in the presence of an insufficient amount of O_2 (0.13 mM). The mixture of CrO^{2+} and CrO_2^{2+} was generated by stopped-flow mixing of 0.08 mM Cr^{2+} with O_2. The Cr^{2+} product from the reaction of CrO^{2+} with CH_3OH consumes CrO_2^{2+} autocatalytically. $[HClO_4] = 0.10$ M, 25 °C, path length = 2 cm.

Stopped-flow mixing of 0.3 mM Cr^{2+} with 1.2 mM O_2 in the presence of 0.06-0.6 M CH_3OH gives rise to first-order absorbance increases at 290 nm, identical to the traces obtained by syringe transfer of reagents. When the O_2 concentration was lowered to 0.26 mM, a biphasic trace appeared, Figure 4. The formation of CrO_2^{2+} from the reaction of CrO^{2+} with CH_3OH begins as before, but O_2 is quickly consumed. The Cr^{2+} product then reacts with the CrO_2^{2+}, causing the absorbance to decrease autocatalytically.

The reaction of CrO^{2+} with CH_3OH can also be studied in the visible region at 417 or 610 nm in the presence of the kinetic probe $ABTS^{2-}$ and excess O_2. Both CrO^{2+} and CrO_2^{2+} are formed in the stopped-flow mixing of Cr^{2+} and O_2, with or without CH_3OH, and both species oxidize $ABTS^{2-}$ at an appreciable rate, as in eqs 3 and 4. The biphasic formation of $ABTS^{\bullet-}$ in the absence of CH_3OH gave $k_5 = (7.9 \pm 0.6) \times 10^4$ L mol^{-1} s^{-} and $k_6 = (1.36 \pm 0.11) \times 10^3$ L mol^{-1} s^{-1} at 25 °C in 0.10 M H^+. The product of reaction 4, the hydroperoxo species CrO_2H^{2+}, has been prepared independently[12] and does not oxidize $ABTS^{2-}$ under these conditions.

When the reaction was conducted in the presence of CH_3OH, the rate constant for the faster phase of $ABTS^{\bullet-}$ formation increased, while the magnitude of the associated absorbance change decreased. The rate constant for the reaction of CrO^{2+} with CH_3OH was then obtained from the faster phase by use of the expression $-d[CrO^{2+}]/dt = (k_3[ABTS^{2-}] + k_8[CH_3OH])[CrO^{2+}]$, yielding $k_8 = 22.4 \pm 2.9$ L mol^{-1} s^{-1} at 0.1 M H^+. This compares well with the value 22.7 L mol^{-1} s^{-1} determined directly from the rate of CrO_2^{2+} formation.

Reaction of CrO^{2+} with Other Alcohols. For every alcohol shown in Table I except cyclobutanol, the reaction produced CrO_2^{2+} when conducted in the presence of O_2. The pseudo-first-order rate constants were derived in the same way as for CH_3OH by following the formation of CrO_2^{2+} in the presence of at least a 10-fold excess of the alcohol. The first-order rate constants were plotted against alcohol concentration. In each case, a significant nonzero intercept of 0.01-0.03 s^{-1} appears in these plots. Significant isotope effects were found for CH_3CH_2OH ($k_H/k_D = 2.31$) and $(CH_3)_2CHOH$ ($k_H/k_D = 2.61$) upon deuterium substitution in all the carbon-hydrogen bonds. The ionic strength dependence of the first-order rate constants is shown for $(CH_3)_2CHOH$ in Figure 5. Activation parameters were determined for the reactions of CH_3OH, CD_3OH, and $(CH_3)_2CHOH$ from the temperature dependence of the rate constants (shown for $(CH_3)_2CHOH$ in Figure 6) and are listed in Table II.

The formation of CrO_2^{2+} is taken as evidence that Cr^{2+} is the immediate product of the reaction of CrO^{2+} with these alcohols. In the oxidation of neopentyl alcohol, the product solution was

Table I. Bimolecular Rate Constants for the Oxidation of Alcohols by $CrO^{2+\,a}$

alcohol	k/L mol^{-1} s^{-1}	alcohol	k/L mol^{-1} s^{-1}
CH_3OH	52.2 ± 1.4	$C_6H_5CH_2OH$	56.0 ± 3.6
CD_3OH	15.1 ± 1.7	$C_6H_5CH(OH)CH_3$	29.6 ± 5.6
CH_3CH_2OH	88.4 ± 4.4	$(C_6H_5)_2CHOH$	10.5 ± 0.8
CD_3CD_2OH	41.5 ± 4.2	$(4\text{-}CH_3O)C_6H_4CH_2OH$	71.2 ± 3.6
$(CH_3)_2CHOH$	12.0 ± 0.4	$(4\text{-}CH_3)C_6H_4CH_2OH$	65.6 ± 3.8
$(CD_3)_2CDOH$	4.6 ± 0.2	$(4\text{-}CF_3)C_6H_4CH_2OH$	60.1 ± 1.7
$CH_2{=}CHCH_2OH$	100.7 ± 6.6	cyclobutanol	44.1 ± 1.2
$CH_3(CH_2)_2CH_2OH$	43.8 ± 3.9	cyclopentanol	30.6 ± 0.6
$CH_3CH_2CH(OH)CH_3$	41.4 ± 0.7	$(CH_3)_3CCH_2OH$	39.0 ± 3.3

[a] All rate constants were measured at 25 °C in O_2-saturated aqueous 0.10 M $HClO_4$/0.90 M $LiClO_4$ or 1.0 M $HClO_4$. In each case, CrO^{2+} was generated by the reaction of Cr^{2+} with O_2, and for all but cyclobutanol, the reaction of CrO^{2+} with ROH was monitored using the increase in absorbance at 290 nm due to CrO_2^{2+} formation. For cyclobutanol, the loss of absorbance at 270 nm due to CrO^{2+} was monitored.

Table II. Activation Parameters for the Oxidation of Organic Substrates by Hydride Transfer

		activation parameters		
oxidant	substrate	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	ref
CrO^{2+}	CH_3OH	34 ± 6	−99 ± 20	this work
	CD_3OH	38 ± 7	−95 ± 21	this work
	$(CH_3)_2CHOH$	33 ± 3	−112 ± 14	this work
	cyclobutanol	46 ± 1	−61 ± 2	this work
$Ru(bpy)_2pyO^{2+}$	CH_3OH	58 ± 8	−109 ± 25	33a
	CD_3OH	71 ± 8	−88 ± 20	33a
	CH_3CH_2OH	38 ± 3	−167 ± 8	33a
	$C_6H_5CH_2OH$	24 ± 1	−159 ± 4	33a
	$C_6H_5CD_2OH$	23 ± 3	−192 ± 8	33a
$Ru(trpy)(bpy)O^{2+}$	$(CH_3)_2CHOH$	38 ± 4	−142 ± 17	33b
Ph_3C^+	CH_3CH_2OH	70	−92	34
	$(CH_3)_2CHOH$	60	−109	34

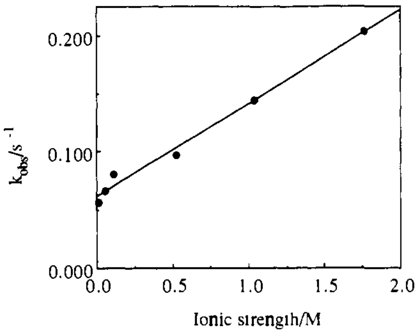

Figure 5. Ionic strength dependence of the observed rate constant for the oxidation of 9 mM $(CH_3)_2CHOH$ by CrO^{2+} at 25 °C. Since there is no dependence of the rate constant on $[H^+]$, the ionic strength was changed by varying either $[HClO_4]$ or $[LiClO_4]$.

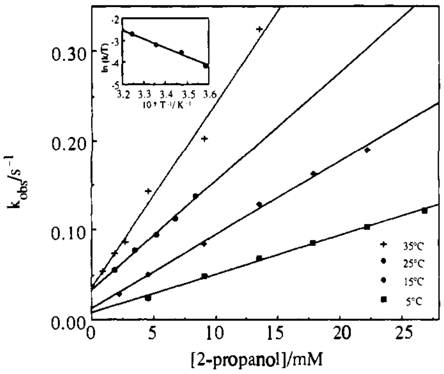

Figure 6. Dependence of the bimolecular rate constant for the oxidation of $(CH_3)_2CHOH$ by CrO^{2+} on temperature. All measurements were made in a 1-cm spectrophotometer cell containing 0.10 M $HClO_4$/0.90 M $LiClO_4$ saturated with O_2. The inset shows a plot of ln (k/T) versus temperature, with slope $\Delta H^\ddagger/R$ = 4007 K^{-1} and intercept $(\Delta S^\ddagger/R)$ + ln (R/Nh) = 10.277.

analyzed for HCHO, a product of the cleavage of the hydroxyneopentyl radical, eq 12. No HCHO was found. The yield of

$$(CH_3)_3CCHOH \rightarrow (CH_3)_3C^\bullet + HCHO \qquad (12)$$

the inorganic product CrO_2^{2+} does not depend on the ionic strength in the range 0.10–1.0 M.

Reaction of CrO^{2+} with Cyclobutanol. This reaction is unlike the reactions with all the other alcohols we studied in that it does not give rise to CrO_2^{2+} in the presence of excess O_2. Also, the reaction is not autocatalytic in the presence of a limiting amount of O_2. The reaction is characterized by an absorbance decrease in the ultraviolet region, corresponding to the loss of CrO^{2+}. First-order kinetic traces were obtained at 270 nm where CrO^{2+} absorbs significantly. The pseudo-first-order rate constants are linearly dependent on the concentration of cyclobutanol, giving a bimolecular rate constant of 44.1 ± 1.2 L mol^{-1} s^{-1} in 1.0 M H^+ at 25 °C. The rate constant is independent of $[H^+]$ and ionic strength in the range 0.10–1.0 M. Activation parameters for the oxidation of cyclobutanol by CrO^{2+} are given in Table II.

Reaction of CrO^{2+} with HCHO and Pivaldehyde. The reaction of 0.1 mM CrO^{2+} with millimolar aqueous HCHO in the presence of O_2 also yields CrO_2^{2+}. The pseudo-first-order rate constants are linearly dependent on the concentration of HCHO, with an intercept of 0.029 s^{-1} and a slope of 91.7 ± 2.9 L mol^{-1} s^{-1} in 0.10 M H^+ (μ = 1.0 M). The bimolecular rate constant is acid-independent in the range 0.10–1.0 M. Activation parameters are $\Delta H^\ddagger$ = 46.8 ± 1.7 kJ/mol and $\Delta S^\ddagger$ = −50 ± 1.9 J/K·mol. The formation of CrO_2^{2+} from CrO^{2+} and 0.6 mM HCHO is not observed in the presence of 1–10 mM Mn^{2+}, a scavenger for CrO^{2+}.[10] Under these conditions an absorbance decrease rather than an increase was recorded at 290 nm. The reaction mixture containing Mn^{2+} developed an intense yellow color and an insoluble precipitate of MnO_2 regardless of whether HCHO was present or not.

The reaction of CrO^{2+} with pivaldehyde, $(CH_3)_3CCHO$, does not yield CrO_2^{2+}. The reaction was studied by monitoring the loss of CrO^{2+} at 260 nm. The second-order rate constant is 37.1 ± 6.4 L mol^{-1} s^{-1} at 25 °C and is acid-independent. CH_4, isobutane, and isobutene were identified as the major organic products by gas-phase chromatography. The other expected organic product, acetone, was not determined.

Reactions of CrO^{2+} with HCO_2H and $H_2C_2O_4$. These reactions give CrO_2^{2+} as the inorganic product in the presence of O_2, regardless of the order of mixing of reagents. At a 1:1 Cr^{2+}:O_2 ratio, the formation of CrO_2^{2+} is followed by an autocatalytic decrease in absorbance, similar to that reported above for the alcohol reactions. When O_2 is in large excess over Cr^{2+}, the increase in absorbance at 290 nm is pseudo first order for all concentrations of excess HCO_2H (0.35–2.8 mM) and $[H_2C_2O_4]$ (0.010–0.024 M). At higher $H_2C_2O_4$ concentrations, mixed first- and second-order traces were obtained. The bimolecular rate constants for both reactions are inversely acid-dependent in the range 0.05 M < $[H^+]$ < 1.0 M. The rate law was resolved into acid-independent and acid-dependent terms using the known acid–base equilibria between the carboxylic acids H_2A and their conjugate bases HA^-

$$k_{obs} = k'[H_2A] + k''[HA^-] + k_d = \frac{k'[H^+] + k''K_a}{K_a + [H^+]}[A]_{total} + k_d \qquad (13)$$

where $K_a = [HA^-][H^+]/[H_2A]$ and $k_d = 0.022$ s^{-1} is the intercept of the plot of k_{obs} versus total carboxylic acid concentration. For HCO_2H, pK_a = 3.53[22] leads to simplification of the rate law, since $[H^+] \gg K_a$. Thus

$$k_{obs} - k_d = \left(k' + \frac{k''K_a}{[H^+]}\right)[A]_{total} \qquad (14)$$

A plot of $(k_{obs} - k_d)/[A]_{total}$ versus $[H^+]^{-1}$ is linear with slope $k''K_a = 2.03 \pm 0.10$ s^{-1}, giving $k'' = (6.68 \pm 0.33) \times 10^3$ M^{-1} s^{-1} as the bimolecular rate constant for the reaction of HCO_2^- with CrO^{2+}. The intercept yields $k' = 11.6 \pm 1.1$ L mol^{-1} s^{-1}.

For $H_2C_2O_4$, pK_{a1} = 1.04 and pK_{a2} = 3.55,[22] so the assumption made in eq 14 is not valid. Therefore, the acid-dependent rate constants k_{obs} were fitted to the complete rate law of eq 13 using a nonlinear least-squares fitting routine and allowing k', k'', and K_a to vary. The fitting routine reproduced the literature value for $K_a = 0.093$ and gave a negligible value for $k' = 68 \pm 81$ L mol^{-1} s^{-1}. With the k' term assumed to be zero, the rate law simplifies to eq 15. A least-squares fit to eq 15 gave $k'' = (2.23$

$$k_{obs} - k_d = \frac{k''K_a}{K_a + [H^+]}[A]_{total} \qquad (15)$$

$\pm\ 0.25) \times 10^3$ L mol^{-1} s^{-1} as the bimolecular rate constant for the oxidation of $HC_2O_4^-$ by CrO^{2+}. Although small amounts of $C_2O_4^{2-}$ may be present in solution, the kinetic data do not require the inclusion of a term in $[H^+]^{-2}$, therefore the reaction of $C_2O_4^{2-}$ with CrO^{2+} is unimportant in the pH range used.

Reaction of CrO^{2+} with $(CH_3CH_2)_2O$. CrO_2^{2+} is formed from CrO^{2+} by its reaction with $(CH_3CH_2)_2O$ in the presence of O_2. The pseudo-first-order rate constants vary linearly with the concentration of $(CH_3CH_2)_2O$, which is the excess reagent. The bimolecular rate constant is 4.45 ± 0.28 L mol^{-1} s^{-1} in 0.10 M H^+ at 25 °C. Tetrahydrofuran does not react with CrO^{2+} under these conditions.

Generation of Air-Free CrO^{2+} from CrO_2^{2+} or $CrOOCr^{4+}$. Stopped-flow mixing of 0.050 mM argon-saturated CrO_2^{2+} with a solution containing 0.025 mM Cr^{2+} and 0.3–2 mM $ABTS^{2-}$ in 0.10 M H^+ causes a biphasic formation of $ABTS^{\bullet-}$ at 417 nm. The rate constant for the fast phase is $(8.4 \pm 1.2) \times 10^4$ L mol^{-1} s^{-1}, in agreement with the rate constant for reaction 3 reported above in the presence of O_2, 7.9×10^4 L mol^{-1} s^{-1}. When CH_3OH was also present, the rate constant of the fast phase was higher due to reaction 8, however, the absorbance change was smaller because reaction 8 does not contribute to the absorbance increase and because some of the Cr^{2+} product reduces $ABTS^{\bullet-}$.

Mixing of 0.0275 mM air-free $CrOOCr^{4+}$ and 0.275–2.06 mM $ABTS^{2-}$ in 0.10 M H^+ was done at 25 °C in the stopped-flow apparatus. The rate of formation of $ABTS^{\bullet-}$ was recorded at 417 nm and fitted to a first-order kinetic equation. The pseudo-first-order rate constants were plotted against the $[ABTS^{2-}]$, giving a straight line with slope $k = 802 \pm 47$ L mol^{-1} s^{-1} and negligible intercept. When the $ABTS^{2-}$ solution contained Cr^{2+}, a biphasic absorbance increase was observed. The rate constant for the slower phase corresponds to the reaction of the remaining $CrOOCr^{4+}$ with $ABTS^{2-}$, while the rate constant measured for the faster phase, 7.1×10^4 L mol^{-1} s^{-1}, corresponds to the reaction between $ABTS^{2-}$ and CrO^{2+} formed in mixing time. The total absorbance change in the presence of Cr^{2+} is only 35% of the absorbance change in the absence of Cr^{2+}, due to consumption of some CrO^{2+} by Cr^{2+} during mixing time, eq 16.

$$CrO^{2+} + Cr^{2+} + H_2O \rightarrow Cr(OH)_2Cr^{4+} \qquad (16)$$

Generation of CrO^{2+} from Cr^{2+} and $TlOH^{2+}$. A solution of 0.22 mM $TlOH^{2+}$ in 0.10 M H^+ was saturated with argon, then 0.22 mM Cr^{2+} was injected. Then an equal volume of O_2-saturated 0.10 M $HClO_4$ containing 0.37–2.34 mM CH_3OH was quickly mixed with the CrO^{2+}-containing solution. The increase in absorbance at λ 290 nm yielded $k_8 = 29.3 \pm 0.8$ L mol^{-1} s^{-1}, in agreement with the values determined by other CrO^{2+}-generating methods at 0.10 M ionic strength. At the end of the reaction, the UV spectrum shows clearly the 290-nm peak of CrO_2^{2+}, produced in ca. 15% yield based on initial $[Cr^{2+}]$. The low yield is again attributed to the loss of CrO^{2+} in reaction 16, which competes effectively with reaction 7 ($k_7 = 2 \times 10^6$ L mol^{-1} s^{-1}).[23] A blank experiment, in which all components except CH_3OH were mixed as described above, showed no formation of CrO_2^{2+}. $TlOH^{2+}$ does not oxidize CH_3OH under these conditions.

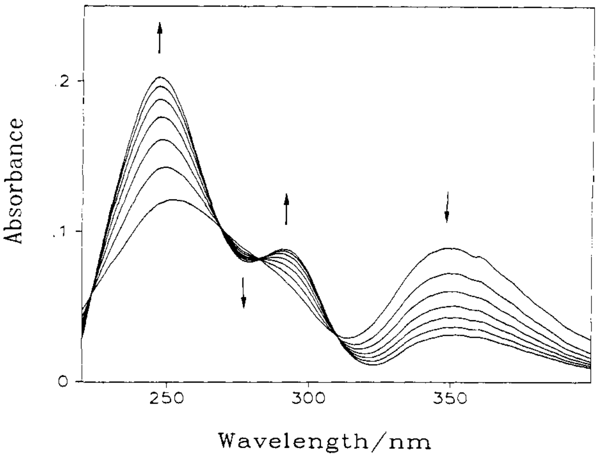

Figure 7. Formation of CrO_2^{2+} (λ_{max} 290, 245 nm) during the oxidation of 0.21 M $(CH_3)_2CHOH$ by 0.069 M $HCrO_4^-$ (λ_{max} 345, 255 nm). The solution contained 2.0 M $HClO_4$ and 1.26 mM O_2. Spectra were recorded at 4-min intervals in a 1-cm cell.

Table III. Yield of CrO_2^{2+} from the Oxidation of 2-Propanol by $HCrO_4^-$ [a]

$[HCrO_4^-]$/mM	yield of CrO_2^{2+}/mM[b]	% yield of CrO_2^{2+}
0.364	0.099 (0.091)	28
0.069	0.042 (0.042)	64
0.042	0.032 (0.030)	76
0.016	0.013 (0.014)	81

[a] Concentrations of $HCrO_4^-$ and CrO_2^{2+} were determined spectrophotometrically. Solutions contained 2 M $HClO_4$, 1.26 mM O_2, and 0.23 M 2-propanol at 25 °C. [b] Values in parentheses are predicted yields from numerical integration using the program KINSIM. Rate constants used in the simulation were $k_{29} = 2 \times 10^9$ L mol^{-1} s^{-1}, $k_9 = 1.6 \times 10^8$ L mol^{-1} s^{-1}, $k_{-9} = 2.5 \times 10^{-4}$ s^{-1}, and $k_{17} = 8 \times 10^8$ L mol^{-1} s^{-1}.

Intermediacy of CrO^{2+} in the Reaction of $HCrO_4^-$ with $(CH_3)_2CHOH$. An O_2-saturated solution containing 0.069 mM $HCrO_4^-$ in 2.0 M $HClO_4$ was allowed to react with 0.21 M $(CH_3)_2CHOH$. The peak in the visible spectrum at 345 nm due to $HCrO_4^-$ decreased in intensity over a period of 5 min, while new peaks at 290 and 245 nm grew in, Figure 7. The final spectrum was that of CrO_2^{2+}. The percent yield of CrO_2^{2+} depends on the initial concentration of $HCrO_4^-$, as shown in Table III, and approaches 100% as the concentration of $HCrO_4^-$ is lowered.

Discussion

Reaction of Cr^{2+} with O_2. This is a complex, multistep reaction. The first step was identified by pulse radiolysis[16] as formation of a 1:1 adduct between O_2 and Cr^{2+}. The adduct, CrO_2^{2+}, was described as a superoxochromium(III) because of its electronic spectrum, its kinetic stability, and its thermodynamic stability constant.[15] Subsequent steps in the reduction of O_2 by Cr^{2+} are not well-established, because they are extremely rapid. For example, the reaction of CrO_2^{2+} with Cr^{2+} is too rapid for conventional stopped-flow mixing, although an estimate of the rate constant (8×10^8 L mol^{-1} s^{-1}) was obtained from analysis of the homolysis kinetics of CrO_2^{2+}.[15] The ultimate product of the Cr^{2+} + O_2 reaction is known to be $Cr(OH)_2Cr^{4+}$,[24] formed when Cr^{2+}

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(22) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1977; Vol. 3, pp 1 and 92.

(23) Dulz, G. E. Ph.D. Thesis, Columbia University, 1963.

enters the coordination sphere of Cr(IV) and is then oxidized. After electron transfer, both metal centers become Cr(III), in which the coordination spheres are frozen. Therefore the bis-μ-hydroxo dimer is produced, rather than $Cr(H_2O)_6^{3+}$. One proposal[15] for the complete mechanism is shown in Scheme I, although we will now revise certain features of it.

Scheme I

$$Cr^{2+} + O_2 \rightleftharpoons CrO_2^{2+} \tag{9}$$

$$CrO_2^{2+} + Cr^{2+} \rightarrow CrOOCr^{4+} \tag{17}$$

$$CrOOCr^{4+} + Cr^{2+} + H_2O \rightarrow Cr(OH)_2Cr^{4+} + CrO^{2+} \tag{6}$$

$$CrO^{2+} + Cr^{2+} + H_2O \rightarrow Cr(OH)_2Cr^{4+} \tag{16}$$

Both $CrOOCr^{4+}$ and CrO^{2+} are proposed intermediates in the oxidation of Cr^{2+} by O_2, and both are now known in other reactions as well. Since k_{17} is very large, reaction 17 competes with 9 when the concentrations of CrO_2^{2+} and O_2 are comparable. However, no real evidence has ever been found in this or in previous work for the intermediacy of $CrOOCr^{4+}$. Therefore, we must consider that (a) $CrOOCr^{4+}$ is not stable enough to be observed or isolated, (b) $CrOOCr^{4+}$ reacts with Cr^{2+} much more rapidly than CrO_2^{2+} does, or (c) $CrOOCr^{4+}$ is not formed. The first option is ruled out by the independent preparation[21] of $CrOOCr^{4+}$ by the reaction of CrO_3 and H_2O_2, which demonstrated that the $CrOOCr^{4+}$ is stable for several minutes at room temperature. It also has a characteristic and fairly intense UV–visible spectrum. The second option seems unlikely because the $Cr^{2+} + CrO_2^{2+}$ reaction is already so fast as to be nearly diffusion-controlled, and the reduction of $CrOOCr^{4+}$ by Cr^{2+} could not be significantly faster. In fact, it may be much slower if the sluggishness of the reaction between Cr^{2+} and H_2O_2 is any guide.[25] The last option seems the most likely then.

The formation of the other intermediate, CrO^{2+}, may be direct, as in

$$CrO_2^{2+} + Cr^{2+} \rightarrow 2CrO^{2+} \tag{18}$$

or indirect, via some other intermediate, for example Cr^VO^{3+}

$$CrO_2^{2+} + Cr^{2+} + H^+ \rightarrow CrO^{3+} + CrOH^{2+} \tag{19}$$

$$CrO^{3+} + Cr^{2+} \rightarrow CrO^{2+} + Cr^{3+} \tag{20}$$

Our observation that the CrO^{2+} generated independently by the reaction of Cr^{2+} with CrO_2^{2+} *in the absence of oxygen* reacts with $ABTS^{2-}$ with the essentially the same rate constant as the intermediate in the reaction of Cr^{2+} with O_2 supports our contention that the same reaction in both systems gives rise to CrO^{2+}. The CrO^{2+} so formed oxidizes alcohols, aldehydes, and some carboxylates, as shown in this work. Aged solutions of initially pure CrO_2^{2+} which contain CH_3OH were also found to contain HCHO, even though CrO_2^{2+} does not react with CH_3OH directly. This observation is easily accounted for by reactions 18 or 19 and 20, since homolysis of CrO_2^{2+} produces the Cr^{2+} needed to produce CrO^{2+}.

Our belief that the oxidant in these reactions contains Cr in the unusual +4 oxidation state, and that this species undergoes two-electron reduction to Cr^{2+}, results from the following reasoning. We consider the possible oxidizing Cr species which could be present in the reaction mixture:

(a) Cr^{VI} would be present as $HCrO_4^-$ under our concentration and pH conditions. This can be detected spectrophotometrically by its absorption maximum at λ 345 nm ($\epsilon = 1.4 \times 10^3$ M^{-1} cm^{-1}), and it was not observed. Although $HCrO_4^-$ is known to oxidize alcohols, the reaction is very slow at pH 1. The intermediate we have studied is certainly a more facile oxidant than $HCrO_4^-$.

(b) Aqueous Cr^V is believed to oxidize alcohols by a two-electron path and/or disproportionate.[9] If it reacts directly with the alcohol, the products must be Cr(III) and a ketone/aldehyde. No combination of these products can possibly give rise to CrO_2^{2+}. If Cr^V disproportionates, one product must be $HCrO_4^-$, which was not observed.

(c) Cr^{IV} is believed to be a strong oxidant that reacts with a variety of alcohols and other organic substrates. These reactions have traditionally been written as one-electron hydrogen-atom abstractions[26] because of the kinetic isotope effects and the stability of the Cr(III) product. However, if Cr^{3+} and a carbon-centered radical are the immediate products of the reaction, then Cr^{3+} must be reduced to Cr^{2+} by the radical in order to form the ultimate product, CrO_2^{2+}. While it is thermodynamically possible for a hydroxyalkyl radical to reduce $Cr(H_2O)_6^{3+}$

$$Cr(H_2O)_6^{3+} + e^- \rightarrow Cr^{2+}_{aq} \qquad E^\circ = -0.416\text{ V} \tag{21}$$

$$CH_2O + H^+ + e^- \rightarrow {}^\bullet CH_2OH \qquad E^\circ = -0.83\text{ V}^{27} \tag{22}$$

this reaction has been shown not to occur[28] because of the reluctance of $Cr(H_2O)_6^{3+}$ to undergo outer-sphere electron transfer and the substitutional inertness of $Cr(H_2O)_6^{3+}$, which prohibits an inner-sphere path. We conclude therefore that the only possible way to obtain Cr^{2+}, and consequently CrO_2^{2+}, is by a two-electron reduction of a Cr(IV) species.

Reaction of CrO^{2+} with Alcohols. The rate constants for the reaction of CrO^{2+} with various alcohols are remarkable in their uniformity. The reactivity of alcohols toward one-electron oxidants such as Ce(IV) varies widely according to the ease of formation of the corresponding hydroxyalkyl radicals: the range of second-order rate constants spans several orders of magnitude.[29] For the reactions studied here, not only is the range of rate constants relatively small but the reactivity order is unconventional. CH_3OH is invariably more difficult to oxidize than $(CH_3)_2CHOH$ by a one-electron (hydrogen-atom-abstraction) path: DH°_{298} (R–H) = 95.9 ± 1.5 kcal/mol for CH_3OH; 90.7 ± 1.1 kcal/mol for $(CH_3)_2CHOH$ (DH° is the bond dissociation energy for the gas-phase reaction $RH \rightarrow R^\bullet + H^\bullet$).[30] However, the thermodynamic properties of the two-electron oxidations are very similar: ΔH°_f(ketone) − ΔH°_f(alcohol) = 17.0 kcal/mol for CH_3OH and 16.75 kcal/mol for $(CH_3)_2CHOH$.[31] Also, the formation of the diphenylhydroxymethyl radical is thermodynamically more favorable than the formation of the phenylhydroxymethyl radical because of the additional benzylic stabilization, yet benzyl alcohol reacts with CrO^{2+} faster than does diphenylmethanol. The lack of a significant para-substituent effect in the oxidation of substituted benzyl alcohols also implies that benzyl radicals are not formed in the oxidation process. Hammett ρ values for processes involving these radicals are generally large and negative, for example −2.0 with Ce(IV) as the oxidant.[14] Therefore we conclude that the oxidation of these alcohols by CrO^{2+} does not proceed by alkyl radical formation.

Instead, we propose that the reactions with alcohols take place by a concerted, two-electron hydride transfer mechanism

$$CrO^{2+} + R_2CHOH \rightarrow [CrO\cdots H\cdots CR_2OH]^{2+} \rightarrow CrOH^+ + R_2CO + H^+ \tag{23}$$

Although this mechanism has not received much attention in the

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[24] Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197. Kolaczkowski, R. W.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 322.

[25] Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 779.

[26] Rahman, M.; Roček, J. *J. Am. Chem. Soc.* **1971**, *93*, 5455, 5462.

[27] Based on $E^\circ({}^\bullet CH_2OH/CH_3OH)$ = 1.29 V (Endicott, J. F. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Ed.; Wiley: New York, 1975; p 88) and $E^\circ(CH_2O/CH_3OH)$ = 0.232 V (Galus, Z. In *Standard Potentials in Aqueous Solution*; Bard, A. J., Ed.; Dekker: New York, 1985; p 197).

[28] The reaction between $Cr(H_2O)_6^{3+}$ and ${}^\bullet C(CH_3)_2OH$ is so slow (k = 5.6 × 10^2 L mol^{-1} s^{-1}) that it is barely detectable (Muralidharan, S.; Espenson, J. H. *Inorg. Chem.* **1984**, *23*, 636). The reduction of $Cr(H_2O)_6^{3+}$ by ${}^\bullet CO_2^-$ was not observed (Ellis, J. D.; Green, M.; Sykes, A. G.; Buxton, G. V.; Sellers, R. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1724).

[29] Wiberg, K. B. In *Oxidation in Organic Chemistry*; Academic: New York, 1965; Part A. Meyer, K.; Roček, J. *J. Am. Chem. Soc.* **1972**, *94*, 1209. Littler, J. S. *J. Chem. Soc.* **1959**, 4135.

[30] Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

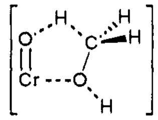
[31] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic Compounds*; Academic: London, 1970; pp 200–202.

literature, it would seem to be thermodynamically preferable to the previously-proposed hydrogen-atom transfer reaction, eq 24.

$$CrO^{2+} + CH_3OH \rightarrow CrOH^{2+} + {}^{\bullet}CH_2OH \quad (24)$$

The additional energy required to form $CrOH^+$ rather than $CrOH^{2+}$ is more than compensated by the formation of the stable aldehyde (or ketone) instead of the highly-energetic hydroxyalkyl radical. The standard potential for the Cr(IV)/Cr(III) couple is unknown, although estimates as high as 2.0 V have been made.[32] However, the difference of free energies, $\Delta G^\circ_{23} - \Delta G^\circ_{24}$, does not depend on this potential. Taking into account the protonation states of the chromium products, $CrOH^+$ and $CrOH^{2+}$, we estimate the free energy difference as −28 kJ/mol. Therefore the hydride transfer path is more favorable than the hydrogen-atom transfer path by 28 kJ/mol. This difference is not so large, however, as to preclude the hydrogen-atom transfer path when an especially stable alkyl radical is formed. Other possible mechanisms are proton-coupled electron transfer via the hydroxyl group, ruled out on the basis of the absence of a solvent isotope effect, and outer-sphere electron transfer which is unlikely because of the high energies of the protonation states of both products (CrO^+ and ROH^-) which would result.

The moderate primary isotope effects (CH_3OH/CD_3OH, 3.46; C_2H_5OH/C_2D_5OH, 2.13; C_3H_7OH/C_3D_7OH, 2.61) support the direct involvement of the carbon–hydrogen bond in the rate-determining step. The effects are not as large as for the $Ru(bpy)(py)O^{2+}$ oxidation of alcohols,[33] which range from $k_H/k_D = 9$ for CH_3OH/CD_2OH to 50 for $C_6H_5CH_2OH/C_6H_5CD_2OH$ and for oxidation by RuO_4 ($k_H/k_D = 4.6 \pm 0.2$ with 2-propanol-*2-d*)[34] which are all claimed to proceed by hydride mechanisms. Isotope effects are smaller for the known hydride transfers between Ph_3C^+ and $(CH_3)_2CHOH$ ($k_H/k_D = 1.84$) and HCO_2^- ($k_H/k_D = 2.5$).[35] Quantum mechanical tunneling has been invoked to explain the largest primary isotope effects. However, even the magnitude of the smaller isotope effects depends strongly on the geometry of the transition state, being greatest when the C–H–O system is linear. Since the RuN_5O^{2+} complexes are substitutionally inert, and there is little likelihood of coordination-sphere expansion, the transition state for hydride abstraction is probably linear. However, MO analysis[36] has shown that the activation energy for hydride transfer from methanol to the oxo ligand of RuN_5O^{2+} would be substantially lowered by prior coordination of the substrate to the metal via the hydroxylic oxygen. Such an intermediate in the CrO^{2+} reaction with CH_3OH would have the following structure:



Formation of a side-on hydrogen bond rather than a linear hydrogen bond minimizes the repulsion between the C–H bond and the oxo lone pair. The cyclic intermediate will certainly exhibit smaller isotope effects than a linear transition state. Since Cr(IV) is substitutionally labile,[11] it is plausible that alcohols, aldehydes, and carboxylic acids coordinate to CrO^{2+} before being oxidized. Analogous esters have been identified in the reactions between $HCrO_4^-$ and alcohols in nonaqueous solvents.[8] Prior coordination may explain why alcohols that are sterically hindered react more slowly (e.g. $(CH_3)_2CHOH$ vs CH_3CH_2OH and $(C_6H_5)_2CHOH$ vs $C_6H_5CH_2OH$).

The intercepts in all the plots of k_{obs} versus [ROH] are small, reproducible, and do not depend in any apparent way on the nature of the alcohol. We believe that this feature, a CrO^{2+}-consuming process with a first-order rate constant of ca. 0.030 s^{-1} in 1.0 M $HClO_4$ and 0.015 s^{-1} in 0.10 M $HClO_4$, represents the spontaneous decomposition of CrO^{2+}. If alcohol addition to the CrO^{2+}-containing solution was delayed by a few minutes, no CrO_2^{2+} was formed. Both observations are easily explained if CrO^{2+} decomposes on this time scale. We have not yet fully explored the products and mechanism of this side reaction. A likely possibility is bimolecular disproportionation of CrO^{2+}, ultimately yielding $HCrO_4^-$ and Cr^{3+}. Further studies of this reaction are in progress.

The substantial ionic strength effect for the reaction of CrO^{2+} with alcohols was unexpected, since one of the reactants is uncharged. We do not have a satisfactory explanation for this phenomenon at present. We speculate that the strong trans-labilizing effect of the oxo group induces an equilibrium between five- and six-coordinate forms of the $(H_2O)_nCrO^{2+}$ ion, $n = 4$ or 5, and that the ratio of the two forms of CrO^{2+} is affected by variations in ionic strength.

Activation Parameters. Values are shown in Table II for the oxidations of CH_3OH, CD_3OH, $(CH_3)_2CHOH$, and cyclobutanol by CrO^{2+}. Parameters for other reactions known to be hydride transfers are also shown in Table II for comparison. Hydride transfers are generally characterized by positive values of $\Delta H^\ddagger$ and large negative values of $\Delta S^\ddagger$. The latter have been attributed to the strict orientational requirements for hydride transfer. In the CrO^{2+} system, collinearity is not required, but formation of a complex between CrO^{2+} and ROH and achievement of the cyclic transition state would certainly contribute to a large negative value of $\Delta S^\ddagger$.

Reaction of $HCrO_4^-$ with Alcohols and Cr^{2+}. The currently accepted mechanism[26] for the oxidation of alcohols by $HCrO_4^-$ involves Cr(IV), but not Cr^{2+}, as in Scheme II. However, CrO_2^{2+} formation during the oxidation of $(CH_3)_2CHOH$ by $HCrO_4^-$ requires the intermediacy of Cr^{2+}. The variation in the yield of CrO_2^{2+} can reasonably be ascribed to a competition between $HCrO_4^-$ and O_2 for Cr^{2+}, as in eqs 29 and 9. The rate constant

Scheme II

$$HCrO_4^- + R_2CHOH \rightarrow Cr^{IV} + R_2CO + 2H^+ \quad (25)$$

$$Cr^{IV} + R_2CHOH \rightarrow Cr^{3+} + R_2\dot{C}OH + H^+ \quad (26)$$

$$HCrO_4^- + R_2\dot{C}OH \rightarrow Cr^{V} + R_2CO + H^+ \quad (27)$$

$$2Cr^{V} \rightarrow HCrO_4^- + Cr^{IV} \quad (28)$$

$$Cr^{2+} + HCrO_4^- \rightarrow Cr^{3+} + Cr^{V} \quad (29)$$

k_{29} is too large to measure using conventional stopped-flow techniques.[6] Using the known value of $k_9 = 1.6 \times 10^8$ L mol^{-1} s^{-1},[15] rate constant k_{29} was derived from the yields of CrO_2^{2+} in Table III by eq 30:[37]

$$\frac{k_{29}}{k_9} = \frac{[O_2] \ln ([HCrO_4^-]_0/[CrO_2^{2+}]_\infty)}{[CrO_2^{2+}]_\infty} \quad (30)$$

The derived value for k_{29} is $(2.0 \pm 0.6) \times 10^9$ L mol^{-1} s^{-1} in 2.0 M $HClO_4$. The yields of CrO_2^{2+} are well predicted by kinetic simulation using this value for k_{29} (see Table III). Because the yield of CrO_2^{2+} approaches 100% as the concentration of $HCrO_4^-$ decreases, we rule out oxidation of CrO^{2+} by $HCrO_4^-$, a reaction which has been proposed in the literature[10] even though it is thermodynamically uphill. The possible disproportionation[10,38] of CrO^{2+} also does not seem important in the presence of a large excess of alcohol.

The two-electron reaction of CrO^{2+} with aliphatic alcohols is incorporated into Scheme III, which we believe should supersede the model in Scheme II. The precise formula of the Cr^V in-

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Scheme III

$$HCrO_4^- + R_2CHOH + 3H^+ \rightarrow CrO^{2+} + R_2CO + 3H_2O \quad (25)$$

$$CrO^{2+} + R_2CHOH \rightarrow Cr^{2+} + R_2CO + H_2O \quad (31)$$

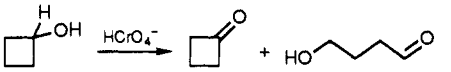
$$HCrO_4^- + Cr^{2+} \rightarrow Cr^{V} + Cr^{3+} \quad (29)$$

$$2Cr^{V} \rightarrow HCrO_4^- + CrO^{2+} \quad (28)$$

termediate is unknown. Scheme III does not contradict previous observations (no polymerization of acrylonitrile and no kinetic effect of O_2),[39] because radicals are not produced and Cr^{2+} reacts with $HCrO_4^-$ even more rapidly than it does with O_2.

Oxidation of 1,2-Diarylethanols and Cyclobutanol. The presence of organic oxidative cleavage products when $HCrO_4^-$ oxidizes a 1,2-diaryl- or 1,2-arylalkylethanol,[14] eq 32, or cyclobutanol,[40] eq 33, has been interpreted as evidence for a one-electron oxidation by CrO^{2+}. Oxidative cleavage is characteristic of one-electron oxidants such as Ce(IV).[40] In previous work on Cr(IV) oxidations,[39] cyclobutanol was the only alcohol studied which did not show a primary isotope effect, leading the authors to conclude that C–C bond cleavage is rate-determining. In the present study, cyclobutanol again behaves differently from all the other alcohols, because its reaction with CrO^{2+} does not yield Cr^{2+}. Also, the activation parameters for the cyclobutanol reaction are different, with larger $\Delta H^{\ddagger}$ and smaller $\Delta S^{\ddagger}$ compared to the values in other alcohol reactions, Table II.

$$ArCH(OH)CH_2Ar' \xrightarrow{HCrO_4^-} ArC(O)CH_2Ar' + (ArCHO + Ar'CH_2OH) \quad (32)$$


(33)

In order to reconcile these observations with the proposed mechanism in eq 23, we consider two alternatives. Oxidative cleavage may result from a two-electron process; such reactions have been documented[41] but only when especially stable organic cations are formed. Two-electron oxidative cleavage of cyclobutanol would be unprecedented. Alternately, the CrO^{2+} may be capable of either one-electron or two-electron oxidation, depending on the organic reactant. For simple primary and secondary alcohols, and even benzylic alcohols, formation of Cr^{2+} instead of Cr^{3+} is less expensive than production of alkyl radicals and is favored by the stability of the aldehyde or ketone products. If the product ketone would be highly strained, as in the case of cyclobutanone, or if the potential alkyl radical can be stabilized by multiple benzylic interactions, then Cr^{3+} and a hydroxyalkyl radical are formed instead. The change in mechanism is signaled by a change in the measured activation parameters, since hydrogen-atom transfer reactions usually have larger $\Delta H^{\ddagger}$ and smaller $\Delta S^{\ddagger}$ values than do hydride transfer reactions.[31] We submit that cleavage of cyclobutanol by a given oxidant does not indicate that all reactions of that oxidant are one-electron processes, as was previously suggested.[40] Indeed it seems only that one is. However, in the case of CrO^{2+} oxidations, the presence or absence of the CrO_2^{2+} product is definitive in determining the mechanism.

Oxidation of $(CH_3CH_2)_2O$. A unique property of hydride-abstracting reagents is the ability to oxidize ethers. While one-electron (hydrogen-atom abstraction) oxidation of an ether is very difficult compared to one-electron oxidation of a similar alcohol, hydride abstraction is feasible from both alcohols and ethers.[42] The oxidation of diisopropyl ether by MnO_4^- proceeds by hydride abstraction at almost the same rate as the oxidation of isopropyl alcohol.[43] We have found that CrO^{2+} oxidizes $(CH_3CH_2)_2O$ 20 times more slowly than CH_3CH_2OH but only 2.7 times more slowly than $(CH_3)_2CHOH$.

Reaction of CrO^{2+} with Aldehydes. The oxidation of aldehydes by H_2CrO_4[44] and Cr(IV)[45] has already been studied in some detail. The $HCrO_4^-$ oxidation of HCHO induces the oxidation of Mn^{2+} with an induction factor (ratio of moles of Mn^{2+} oxidized to moles of aldehyde oxidized) of 0.5, implying that Cr(IV) is a reactive intermediate. The fate of Cr(IV) may have been oxidation by H_2CrO_4, one-electron oxidation of HCHO yielding Cr^{3+}, or two-electron oxidation of HCHO to yield Cr^{2+}. No evidence was then available to distinguish between these alternatives. In the more recent study,[45] the reaction of $HCrO_4^-$ with VO^{2+} was used to generate Cr(IV) in situ. Addition of an aldehyde to the reaction mixture decreases the yield of VO_2^+ without affecting the rate of loss of $HCrO_4^-$, which led the authors to conclude that the aldehyde reacts only with Cr(IV) and not with Cr(V). On the basis of the relative reactivity of various aldehydes, it was shown that aldehydes react exclusively in their hydrated forms. Since HCHO is essentially completely hydrated in aqueous solution ($K = 1.8 \times 10^3$),[46] the rate constant measured in this work, 91.7 L mol^{-1} s^{-1}, is the rate constant for the reaction between CrO^{2+} and $CH_2(OH)_2$. The mechanism of oxidation is hydride abstraction based on the observation of the inorganic product CrO_2^{2+}. The organic product is inferred to be HCOOH.

The reaction of pivaldehyde with CrO^{2+} in the presence of O_2 does not yield CrO_2^{2+} but does give large amounts of radical cleavage products. A one-electron oxidation followed by elimination of CO from the pivaloyl radical seems to be favored in this case, as in reactions 34 and 35. The fate of the *tert*-butyl radical depends on the O_2 concentration. At low or zero $[O_2]$, the radical disproportionates to isobutane and isobutene. In oxygenated solutions the *tert*-butyl peroxyl radical is formed, which then decomposes bimolecularly to the *tert*-butoxyl radical.[47] This radical fragments to acetone and methyl radical, and the latter abstracts a hydrogen atom from pivaldehyde to become methane.

$$CrO^{2+} + (CH_3)_3CCHO \rightarrow CrOH^{2+} + (CH_3)_3CCO \quad (34)$$

$$(CH_3)_3CCO \rightarrow (CH_3)_3C^{\bullet} + CO \quad (35)$$

Reaction of CrO^{2+} with HCO_2H and $H_2C_2O_4$. The formation of CrO_2^{2+} in both of these reactions implies a two-electron, hydride-transfer mechanism. The inverse acid-dependence is consistent with direct formation of CO_2 from HCO_2^- and $HC_2O_4^-$, as in eqs 36 and 37. The rate constants k_{36} and k_{37} are much larger than the rate constants for oxidation of HCO_2H and $H_2C_2O_4$. This is partly due to the increased equilibrium constant for formation of the precursor complex from oppositely-charged ions. In addition, the product, CO_2, is formed directly from HCO_2^- and $HC_2O_4^-$ in the correct protonation state; therefore the energy of the transition-state is lowered by the preequilibrium loss of a proton. The second-order dependence on $H_2C_2O_4$ observed at high $[H_2C_2O_4]$ may be due to association of $H_2C_2O_4$ in solution; such interactions have been previously noted.[48]

$$CrO^{2+} + HCO_2^- \rightarrow CrOH^+ + CO_2 \quad (36)$$

$$CrO^{2+} + HC_2O_4^- \rightarrow CrOH^+ + 2CO_2 \quad (37)$$

Summary

CrO^{2+} is a versatile oxidant with a half-life of ca. 30 s in 1.0 M $HClO_4$ at 25 °C. It oxidizes alcohols, aldehydes, and carboxylates by a two-electron mechanism in all cases except for

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J. Am. Chem. Soc. **1992,** *114,* 4213-4219

cyclobutanol, where cleavage of the strained four-membered ring is favored, and pivaldehyde, where elimination of CO from the pivaloyl radical is preferred.

The rate constants for all the alcohol and aldehyde reactions studied here are very similar, and the reactivity trends are inconsistent with the formation of alkyl radicals. The rate of oxidation of R_2CHOH to R_2CO depends slightly on the steric bulk of R, which suggests that prior coordination of the alcohol to CrO^{2+} may be required before hydride transfer occurs.

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Registry No. CrO^{+2}, 136301-85-4; CH_3OH, 67-56-1; D_2, 7782-39-0; CH_3CH_2OH, 64-17-5; $(CH_3)_2CHOH$, 67-63-0; $CH_2{=}CHCH_2OH$, 107-18-6; $CH_3(CH_2)_2CH_2OH$, 71-36-3; $CH_3CH_2CH(OH)CH_3$, 78-92-2; $C_6H_5CH_2OH$, 100-51-6; $C_6H_5CH(OH)CH_3$, 98-85-1; $(C_6H_5)_2CHOH$, 91-01-0; $(4\text{-}CH_3O)C_6H_4CH_2OH$, 105-13-5; $(4\text{-}CH_3)C_6H_4CH_2OH$, 589-18-4; $(4\text{-}CF_3)C_6H_4CH_2OH$, 349-95-1; $(CH_3)_3CCH_2OH$, 75-84-3; HCO_2H, 64-18-6; $H_2C_2O_4$, 144-62-7; $(CH_3CH_2)_2O$, 60-29-7; CrO_2^{+2}, 34021-34-6; Cr^{+2}, 22541-79-3; O_2, 7782-44-7; $CrOOCr^{+4}$, 136301-86-5; $TlOH^{+2}$, 15823-78-6; $HCrO_4^-$, 15596-54-0; cyclobutanol, 2919-23-5; cyclopentanol, 96-41-3; formaldehyde hydrate, 53280-36-7; pivaldehyde, 630-19-3.

Chemistry of an (η^6-Metallabenzene)metal Complex, $[(\eta^6\text{-}\overline{\text{Ir}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{C}}\text{H})(\text{PEt}_3)_3]\text{Mo(CO)}_3$[1]

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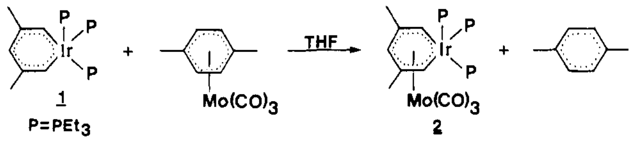
Contribution from the Department of Chemistry, Washington University, St. Louis, Missouri 63130. *Received September 20, 1991*

Abstract: "Iridabenzene", $(\overline{\text{Ir}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{C}}\text{H})(\text{PEt}_3)_3$ (**1**), displaces *p*-xylene from (η^6-*p*-xylene)$Mo(CO)_3$ in tetrahydrofuran solvent, producing (η^6-iridabenzene)$Mo(CO)_3$ (**2**). The solid state structure of **2** has been determined by a single-crystal X-ray diffraction study (monoclinic, $P2_1/n$, $a = 9.897$ (1) Å, $b = 16.213$ (3) Å, $c = 20.937$ (3) Å, $\beta = 96.68$ (1)°, $V = 3336.7$ (9) Å^3, $Z = 4$, $R = 0.036$, $R_w = 0.042$). The iridium center in **2** retains the square-pyramidal coordination geometry of parent compound **1**, but the $Mo(CO)_3$ moiety now occupies the formerly "open face" of the pyramid. In solution, the iridabenzene ring rotates with respect to the $Mo(CO)_3$ fragment. The barrier for this process ($\Delta G^\ddagger$) is estimated to be less than 8 kcal/mol. Treatment of **2** with PMe_3 or CO (L) results in clean replacement of one basal PEt_3 ligand and production of $[(\eta^6\text{-}\overline{\text{Ir}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{C}}\text{H})(\text{PEt}_3)_2(\text{L})]\text{Mo(CO)}_3$ (**3**, L = PMe_3; **4**, L = CO). The solid state structure of **3** (monoclinic, $P2_1/n$, $a = 10.005$ (2) Å, $b = 18.012$ (3) Å, $c = 17.055$ (4) Å, $\beta = 93.33$ (2)°, $V = 3068.3$ (11) Å^3, $Z = 4$, $R = 0.031$, $R_w = 0.041$) confirms the basal coordination position of the PMe_3 ligand. As in **2**, solution-phase arene ring rotation in **3** and **4** is facile. Treatment of **2–4** with $HBF_4{\cdot}OEt_2$ leads to protonation of the metal centers and production of the novel μ-H heterobimetallic complexes, $\{[(\eta^6\text{-}\overline{\text{Ir}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{C}}\text{H})(\text{PEt}_3)_2(\text{L})(\mu\text{-H})]\text{Mo(CO)}_3\}^+\text{BF}_4^-$ (**5**, L = PEt_3; **6**, L = PMe_3; 7, L = CO). In the solid state structure of **6**·tetrahydrofuran (orthorhombic, $P2_12_12_1$, $a = 10.200$ (4) Å, $b = 16.467$ (9) Å, $c = 22.023$ (7) Å, $V = 3699$ (3) Å^3, $Z = 4$, $R = 0.022$, $R_w = 0.029$), the hydride ligand resides approximately trans to the axial phosphine on iridium but bends in slightly toward molybdenum, generating a P_{ax}–Ir–H angle of 173 (2)°. The Ir–H and Mo–H bond lengths are 1.77 (6) and 1.97 (7) Å, respectively. While solution-phase arene ring rotation still occurs in **5–7**, the barrier for this process ($\Delta G^\ddagger$) increases to ~13.5–15 kcal/mol.

Introduction

Several years ago we reported the high-yield synthesis of a stable metallabenzene complex, $(\overline{\text{Ir}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{C}}\text{H})(\text{PEt}_3)_3$ (**1**).[1b,2] The structural and spectroscopic features of this species clearly indicated the presence of an aromatic ring system. Fenske–Hall calculations showed that the π-bonding in this ring involved the participation of an iridium-based d orbital with the set of five carbon-based p orbitals.[3] Recently, we have begun to explore the reaction chemistry of iridabenzene **1** and have discovered that it can be readily coordinated to a $Mo(CO)_3$ moiety, producing $[(\eta^6\text{-}\overline{\text{Ir}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{CH}\overset{..}{-}\text{C(Me)}\overset{..}{-}\text{C}}\text{H})(\text{PEt}_3)_3]\text{Mo(CO)}_3$ (**2**).[1c] In this paper, we describe the structure, spectroscopy, and reactivity of (metallabenzene)metal complex **2** and compare its chemistry to that of the parent complex **1**. Since **1** and **2** represents the first *matched pair* of metallabenzene and (metallabenzene)metal complexes,[4] they afford a unique opportunity for comparative study.

Scheme I



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[2] Metallabenzenes are very rare. Only one other stable metallabenzene complex has been reported. See: Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811,

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