

nm (ϵ 400) for **1** is assigned to the $n(\text{Sn})-5p\pi(\text{Sn})$ transition,¹³ since the spectral feature is similar to those of dimethylsilylene^{14a} and dimethylgermylene,^{14b} which show the $n(\text{metal})-p\pi(\text{metal})$ transition band at around 450 nm with relatively low absorption coefficients.

Whereas both **1** and **2** involve two bulky bis(trimethylsilyl)alkyl substituents as the ligands on tin, the cyclic ligand in **1** works like a helmet, protecting the central tin atom much more effectively than the two Lappert's Januslike ligands¹⁵ in **2**. Additionally, the smaller C-Sn-C angle of **1** than that of **2** may partly be responsible for the stabilization of the monomeric structure due to enhancement of the singlet-triplet energy separation.¹⁶

Although the structural arrangement of several sterically protected low-valent organometallic compounds in the solid state can be provided by the ligand-ligand interactions or packing effects,¹⁷ weak but significant Sn-Sn bonding would be principally responsible for determining the solid-state structure of **2**, where the bonding between the tin atoms may be best described by the double dative bond as originally proposed by Lappert et al.^{7b}

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Supplementary Material Available: X-ray experimental details for **1**, tables of positional parameters, thermal parameters, bond lengths, and bond angles for **1**, and ¹H and ¹³C NMR spectra of **1** (11 pages); listing of observed and calculated structure factors for **1** (22 pages). Ordering information is given on any current masthead page.

(13) The relative intensities of the 370- and 484-nm bands for **1** did not depend on the concentration. In addition, the two bands decayed rapidly with the same rate when the sample was aerated. Therefore, the weak 370-nm band is not caused by artifacts but by the intrinsic electronic transition of **1**, whereas the nature of the transition remains open.

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Preparation and Reactivity of the Aquachromium(IV) Ion

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High-valent metal ions are postulated intermediates in biological^{1a} and synthetic organic^{1b} oxidations. Chromium(IV) is an elusive species, detected in a complex with 2-ethyl-2-hydroxybutyrate,² but definitively characterized only with the tetraphenylporphyrin ligand.³ The latter species contains an oxo ligand similar to the ferryl porphyrins⁴ known in oxidation of organic substrates. Despite several decades of interest,⁵ aquachromium(IV) has never been directly observed. This commu-

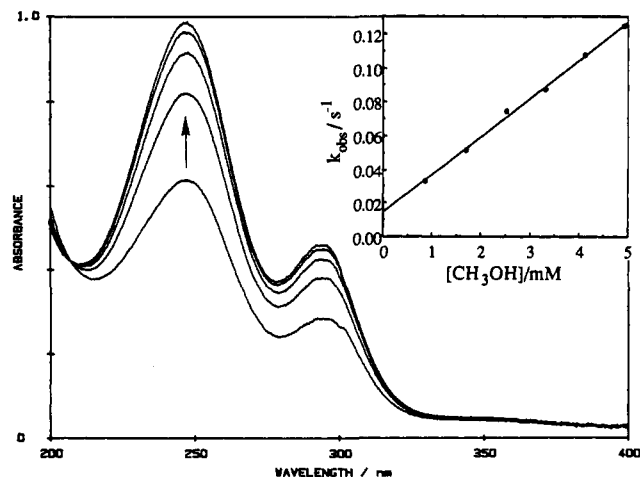
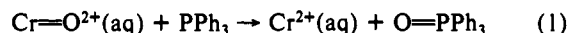


Figure 1. Development of the CrO_2^{2+} spectrum in the reaction between 0.1 mM CrO_2^{2+} and 1.0 mM CH_3OH , in the presence of 1 mM O_2 . The time interval between spectra is 7 s. The inset shows the dependence of the pseudo-first-order rate constants on $[\text{CH}_3\text{OH}]$ at 25 °C in 0.10 M HClO_4 . Slope = 22.7 $\text{L mol}^{-1} \text{s}^{-1}$; intercept = 0.014 s^{-1} .

nication describes four methods for its preparation. In the absence of reducing agents, this species is surprisingly long-lived, with a half-life of 0.75 min at 0.10 M ionic strength at room temperature.

Generation of the new chromium species was accomplished anaerobically by stopped-flow mixing of superoxochromium(III), $\text{CrO}_2^{2+}(\text{aq})$,⁶ or (μ -peroxy)dichromium(III), $\text{CrOOCr}^{4+}(\text{aq})$,⁷ or $\text{Ti}^{\text{III}}(\text{aq})$ with an equal concentration of $\text{Cr}^{2+}(\text{aq})$, 0.1–0.5 mM, in acidic (0.1–1.0 M HClO_4) aqueous solution. Also, mixing $\text{Cr}^{2+}(\text{aq})$ and oxygen, in a 1:1 ratio with stopped-flow mixing or a 1:5 ratio by syringe injection into a spectrophotometer cell, yields chromium(IV). Yields are low (15–50% based on total chromium) because of the competing oxidation of Cr^{2+} by $\text{Cr}(\text{IV})$. The low concentration of $\text{Cr}(\text{IV})$ available by these methods, its lack of significant absorbance in the visible region, and its relatively short lifetime preclude direct characterization of $\text{Cr}(\text{IV})$, which explains why this species has been overlooked despite numerous studies of chromium redox reactions. Therefore, we studied the reactivity of this species in order to identify it (and quantify its yield) and establish its properties.

The chromium(IV) species formed by syringe injection or stopped-flow mixing of Cr^{2+} and O_2 reacts readily with 0.01–0.04 M Ph_3P with rate constant $k = (2.1 \pm 0.2) \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ in 0.10 M $\text{HClO}_4/85\% \text{ CH}_3\text{CN}$ at room temperature.⁸ Under these conditions, reaction 1 is complete in less than 0.2 s; therefore the decomposition of $\text{Cr}(\text{IV})$ does not contribute to the kinetics. The product Ph_3PO is formed quantitatively and was identified by comparison of its UV spectrum with that of an authentic sample. We infer from this that the chromium(IV) exists as an oxo complex, as in the porphyrin complex.³



The immediate addition of millimolar quantities of methanol to oxygenated solutions containing ca. 0.1 mM CrO_2^{2+} , prepared by mixing Cr^{2+} with O_2 , causes the spectrum of CrO_2^{2+} to develop, Figure 1. The equation for this reaction requires O_2 on the reactant side for mass balance, eq 2. The increase in absorbance

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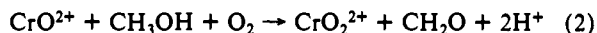
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(6) When $\text{Cr}^{2+}(\text{aq})$ (from Zn/Hg reduction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$) is injected into an acidic aqueous solution containing oxygen at very low $\text{Cr}:\text{O}_2$ ratios, <0.05:1, the adduct CrO_2^{2+} is formed quantitatively (Brynildson, M. E.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4579) with rate constant $1.6 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ (Sellers, R. M.; Semic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6145). The CrO_2^{2+} was identified and quantified by its intense and characteristic UV spectrum, $\epsilon_{290\text{nm}} = 3100 \text{ L mol}^{-1} \text{ cm}^{-1}$, $\epsilon_{245\text{nm}} = 7000 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Ilan, Y. A.; Czapski, G.; Ardon, M. *Isr. J. Chem.* **1975**, *13*, 15).

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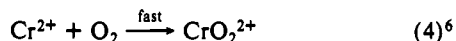
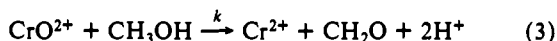


at 290 or 245 nm was fitted to an exponential function, yielding first-order rate constants that are linearly dependent on the concentration of methanol (inset to Figure 1) and independent of $[\text{O}_2]$ (0.26–1.3 mM). The slope, or bimolecular rate constant, is $22.7 \pm 0.6 \text{ L mol}^{-1} \text{ s}^{-1}$ in 0.10 M HClO_4 at 25 °C. The intercept, $0.014 \pm 0.001 \text{ s}^{-1}$, is real and reproducible and is attributed to the methanol-independent decomposition of the CrO^{2+} . Consistent with that, if methanol addition is delayed by a few minutes, the CrO_2^{2+} is no longer formed. The absorbance change for the reaction with methanol was used to estimate the yield of CrO_2^{2+} , ca. 50% based on total Cr.

The rate constant for the oxidation of methanol is independent of $[\text{H}^+]$ (0.02–1.0 M) at constant ionic strength but increases with ionic strength to $52.2 \pm 1.4 \text{ L mol}^{-1} \text{ s}^{-1}$ at 1.0 M ionic strength. (The intercept also increases with ionic strength to $0.033 \pm 0.001 \text{ s}^{-1}$.) A significant deuterium isotope effect was observed for CD_3OH ($k_{\text{H}}/k_{\text{D}} = 3.2$), implicating rate-determining carbon-hydrogen bond breaking. There was no effect of replacing the solvent H_2O by D_2O (which also converted CH_3OH to CH_3OD). Therefore the oxygen-hydrogen bond is not cleaved in the transition state, and the mechanism cannot be proton-assisted electron transfer.

The same reaction was observed for CrO^{2+} prepared from Cr^{2+} and $\text{Ti}^{\text{III}}(\text{aq})$,⁹ first mixed anaerobically in a 1:1 ratio and then added to oxygen-saturated aqueous methanol.¹⁰ CrO^{2+} prepared in this way reacts with methanol with the same rate constant as the CrO^{2+} prepared from Cr^{2+} and O_2 . As before, no CrO_2^{2+} forms without methanol; therefore we exclude the possibility that any Cr^{2+} remaining from the anaerobic step is the cause of the absorbance changes when O_2 is added. In the absence of a reductant such as methanol, no absorbance changes were seen in the UV spectrum; the CrO^{2+} simply decomposes to low-absorbing products. When methanol was present, formaldehyde was identified as a product of the reaction with CrO^{2+} by chromatographic acid analysis.¹¹ CrO^{2+} is also formed when Cr^{2+} and either CrO_2^{2+} or CrOOCr^{4+} are mixed anaerobically. The anaerobic reactions of CrO^{2+} with methanol are not accompanied by absorbance changes due to formation of CrO_2^{2+} , and the Cr^{2+} product reacts rapidly with CrO^{2+} . Studies of other reactions are underway using the CrO^{2+} produced by these methods.

Further evidence that the oxidant is chromium(IV) is found in the methanol reaction, because CrO_2^{2+} is the inorganic product. Since the only known route to CrO_2^{2+} is the combination of oxygen with Cr^{2+} , we infer that it is the immediate product of the reaction. The only oxidant likely¹² to generate Cr^{2+} is $\text{Cr}(\text{IV})$:



If the $\text{Cr}(\text{IV})$ is indeed an oxo species, then the two-electron oxidation of methanol is accomplished by hydride transfer,



followed by rapid proton equilibrations of CrOH^+ and CH_2OH^+ . This mechanism accounts for the observed primary isotope effect and is thermodynamically more favorable than hydrogen atom transfer with formation of chromium(III) and an alkyl radical. Reduction of $\text{Cr}(\text{IV})$ to Cr^{2+} has an estimated potential of +0.84 V, with direct formation of the stable aldehyde, $E^\circ(\text{CH}_3\text{OH}/\text{CH}_2\text{O}) = -0.23 \text{ V}$, whereas reduction of $\text{Cr}(\text{IV})$ to Cr^{3+} has an

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(12) Chromium(III) does not react with methanol; therefore the oxidant must have oxidation state >3 . Chromium(VI) is known to react with alcohols, but very slowly.^{3a} Chromium(V) may disproportionate more rapidly than it reacts with alcohols, but even a two-electron oxidation of methanol by chromium(V) will yield $\text{Cr}(\text{III})$, not $\text{Cr}(\text{II})$.

estimated potential of +2.0 V,¹³ which is offset by the high potential of the radical, $E^\circ(\cdot\text{CH}_2\text{OH}/\text{CH}_3\text{OH}) = +1.29 \text{ V}$.¹⁴ That is, the two-electron path is thermodynamically favored over the one-electron path by 0.26 V. Significant polarization of the carbon-hydrogen bond in the transition state leads to the creation of like charges, which is favored at higher ionic strengths. More studies of the chromium(IV) oxidant as a hydride acceptor and oxo-transfer agent are in progress.

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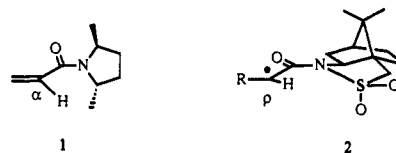
Control of Stereochemistry in Free Radical Reactions with Oxazolidine Auxiliaries

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Recent reports¹⁻⁵ make it clear that control of acyclic stereochemistry is possible in free radical reactions. In the addition of radicals to chiral alkenes, for example, diastereofacial control is possible if the addition occurs α to a center substituted with an amide derived from C_2 symmetric pyrrolidines, e.g. **1**.² Stereochemical control in the addition of chiral radicals to unsaturated systems (ρ selectivity) is also possible if the radical is substituted with a C_2 symmetric pyrrolidine amide³ or an imide derived from camphor sultam, e.g. **2**.⁴ Other radical addition or atom transfer reactions exhibiting significant acyclic α or ρ stereoselectivity have also been recently reported.⁵ Of the auxiliaries used to control acyclic stereochemistry, the dimethylpyrrolidine may give higher selectivities in some reactions but the sultam is commercially available and easy to remove after use.



For α or ρ selectivity with auxiliaries like the C_2 symmetric pyrrolidine or the sultam, the orientation about the $C(\alpha$ or $\rho)$ - $C(\text{O})$ and the $C(\text{O})$ - N bond is critical in fixing the resident chiral group relative to the α or ρ center. For amides and imides, the *Z* orientation is favored for the $C(\alpha$ or $\rho)$ - $C(\text{O})$ bond while C_2 symmetry avoids the need for $C(\text{O})$ - N rotamer control in di-

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