

Reductions of Carboxylate-Bound Chromium(V)

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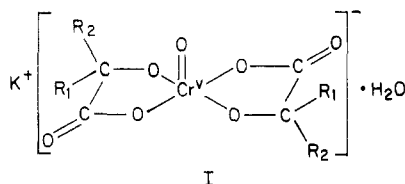
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In 1950, near the beginning of the mid-century renaissance of inorganic chemistry, the chemistry of chromium was centered almost exclusively about the two oxidation states +3 and +6. Chromium(II), (as in CrSO_4), and combined zerovalent chromium (as in $\text{Cr}(\text{CO})_6$), were known but were generally considered chemical curiosities. Shortly thereafter, Cr(II) achieved prominence through Taube's experiments which delineated the mechanisms of electron transfer in solution;¹ and Cr(0) attracted attention through the characterization of bis(benzene)chromium^{2a} and related compounds.^{2b} Remaining were Cr(I) (about which more will be said presently), as well as Cr(IV) and Cr(V).

There has been a recent quickening of interest in the third of these less usual states, Cr(V). Not only is it being investigated by workers dealing with inorganic redox mechanisms, but it has assumed a place in synthetic organic chemistry (both as a stoichiometric oxidant^{3a} and as a catalyst^{3b}), in spectroscopy^{4a} and in magnetochemistry.^{4b} In addition, chromium(V) has not escaped the notice of those examining biosystems.⁵

As early as 1949 Westheimer⁶ described kinetic studies which pointed to the intervention of Cr(IV) and Cr(V) in the oxidation of 2-propanol with CrO_3 , and during the 1960s evidence accumulated⁷ that both of these states were intermediates in the reactions of CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ with such 1st metal-center reductants as Cr(II), Fe(II), V(IV), and Mo(V). Moreover, both Cr(V) and Cr(IV) have yielded to synthetic efforts. Over two dozen Cr(V)-containing compounds,⁸ ranging in complexity from CrF_5 ⁹ to porphyrin derivatives,¹⁰ as well as a less impressive array of Cr(IV) species,¹¹ have now been characterized. However, only a very small number of these are stable in air and dissolve in water without disproportionation (to Cr^{III} and Cr^{VI}).

In 1978, Krumpolc, DeBoer, and Roček^{12a} described the Cr(V) chelate, potassium bis(2-methyl-2-hydroxybutyrate)oxochromate(V) (I: $\text{R}_1 = \text{CH}_3$; $\text{R}_2 = \text{C}_2\text{H}_5$) prepared as a hydrate by treatment of the parent hydroxy acid with CrO_3 , HClO_4 , and KHCO_3 . The



presence of Cr(V) (a d^1 center) in the product was confirmed iodometrically, by magnetic susceptibility and by ESR, whereas the structure of the remainder of the complex was established crystallographically. This

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chelate is stable in air and dissolves readily in water, forming solutions which are stable for hours (provided a bit of the parent acid or its salt is also added). The following year a more convenient and efficient synthesis was reported,^{12b} yielding, as sodium salts, seven additional chelates of type I. The facile preparation of these complexes, the ease with which they could be handled, and, most important, the persistence of Cr(V) in their aqueous solutions combined to make these derivatives particularly attractive candidates for mechanistic studies of the reactions of this oxidation state. For such investigations, the bis(2-ethyl-2-hydroxybutyrate) derivative (I; $\text{R}_1 = \text{R}_2 = \text{C}_2\text{H}_5$), which is the most stable of these chelates, is generally the oxidant of choice. Early work was confined to pH 3-5, within which disproportionation of Cr(V) is minimal, but with rapid reductants, it is possible to work outside this range.

Reduction with Hydrazine.^{12c} Since it was anticipated that Cr(V) would be converted to Cr(III), reducing agents which are thought to react mainly by 2e shifts were chosen for initial experiments. Thallium(I) reacts inconveniently slowly with Cr(V), as do the salts of H_3PO_3 , H_3PO_2 , and H_3AsO_3 , whereas the reaction with SO_3^{2-} is complex, and the kinetic components have only recently been disentangled. However, N_2H_5^+ (the predominant form of hydrazine at pH 3-5) reacts smoothly and, at a readily measurable rate, with the bis(2-ethyl) modification of Cr(V) chelate I. The stoichiometry of this reaction lies very close to 2:1

(1) (a) Taube, H.; Myers, H.; Rich, R. L. *J. Am. Chem. Soc.* 1953, 75, 4118. (b) Taube, H.; Myers, H. *J. Am. Chem. Soc.* 1954, 76, 2103.

(2) (a) Fischer, E. O.; Hafner, W. Z. *Naturforsch. B: Anorg. Chem., Org. Chem., Biochem., Biophys.* 1955, 10B, 665; *Z. Anorg. Allg. Chem.* 1956, 286, 146. (b) Fischer, E. O.; Ofele, K. *Chem. Ber.* 1957, 90, 2532.

(3) (a) Krumpolc, M.; Roček, J. *Inorg. Chem.* 1985, 24, 617. (b) Sammel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* 1985, 107, 7606.

(4) See, for example: (a) Borromei, R.; Oleari, L.; Day, P. *J. Chem. Soc., Faraday Trans. 2* 1979, 75, 401. (b) Roy, A.; Nag, K. *J. Inorg. Nucl. Chem.* 1978, 40, 1501.

(5) Goodgame, D. M. L.; Hayman, P. B.; Hathway, D. E. *Polyhedron* 1982, 1, 497.

(6) Watanabe, W.; Westheimer, F. H. *J. Chem. Phys.* 1949, 17, 61.

(7) See, for example: (a) Espenson, J. H.; King, E. L. *J. Am. Chem. Soc.* 1963, 85, 3328. (b) Sullivan, J. C. *J. Am. Chem. Soc.* 1965, 87, 1495.

(c) Espenson, J. H. *J. Am. Chem. Soc.* 1964, 86, 1883, 5101. (d) Birk, J. P. *J. Am. Chem. Soc.* 1969, 91, 3189. (e) McKnight, G. F.; Haight, G. P. *Inorg. Chem.* 1973, 12, 1619. (f) For critical reviews, see: Espenson, J. H. *Acc. Chem. Res.* 1970, 3, 347. Beattie, J. K.; Haight, G. P. *Prog. Inorg. Chem.* 1972, 17, 93.

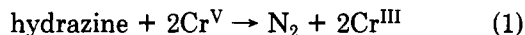
(8) For a recent review, see: Mitewa, M.; Bontchev, P. R. *Coord. Chem. Rev.* 1985, 61, 241. This work also discusses systems in which the reduction of Cr(VI) appears to pass through a Cr(V) intermediate. It is notable for its breadth of coverage of the eastern European literature.

(9) (a) Edwards, A. J. *Proc. Chem. Soc.* 1963, 205. (b) Bougon, R.; Wilson, W. W.; Christie, K. O. *Inorg. Chem.* 1985, 24, 2286.

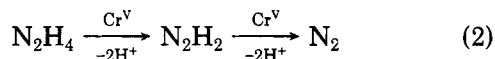
(10) See, for example: (a) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* 1979, 101, 7613. (b) Groves, J. T.; Haushalter, R. C. *J. Chem. Soc., Chem. Commun.* 1981, 1165.

(11) See, for example: (a) Clark, H. C.; Sandana, Y. N. *Can. J. Chem.* 1964, 42, 50. (b) Wilhelmi, K.; Jonson, O. *Acta. Chem. Scand.* 1961, 15, 1415. (c) Hagihara, M.; Yamasaki, H. *J. Am. Chem. Soc.* 1959, 81, 3160. (d) Alyea, E. C.; Basi, J. S.; Bradley, D. C.; Chisholm, M. H. *J. Chem. Soc. A* 1971, 772.

(12) (a) Krumpolc, M.; DeBoer, B. B.; Roček, J. *J. Am. Chem. Soc.* 1978, 100, 145. (b) Krumpolc, M.; Roček, J. *Ibid.* 1979, 101, 3206. (c) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* 1981, 20, 3176.

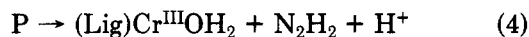
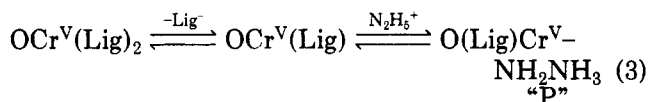


and N_2 is the only nitrogenous product, implying that N_2H_4 is indeed oxidized by a pair of 2e transactions



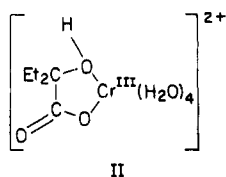
The single-component kinetic curves observed with N_2H_5^+ in excess indicate that the overall rate is determined by the initial step in sequence (2), that is, that the oxidation of diimide, N_2H_2 , is much more rapid than that of hydrazine. Kinetic experiments therefore yield no direct information concerning processes occurring after the first oxidation.

The most notable feature of the rather complex rate law^{12c} for this reaction is an inverse-first-order dependence on the free ligand anion (2-ethyl-2-hydroxybutyrate) added to stabilize the Cr(V) chelate, (i.e., a rate proportional to $1/[\text{Lig}^-]$). This points to a rapid preequilibrium in which one unit of ligand is lost from the oxidant, leaving a coordinatively unsaturated intermediate which can then become attached to N_2H_5^+ prior to the act of electron transfer. The reaction sequence may thus be represented schematically:



The indicated $\text{Cr}^{\text{V}}\text{-N}_2\text{H}_5$ intermediate "P" is analogous to the familiar precursor complex in inner-sphere electron transfers between metal ion centers.¹³

The visible spectrum of the Cr(III) product in this reaction indicates it to be a chelated monocarboxylato species, and its ion-exchange elution behavior is that of a 2+ ion. The product may thus be assigned structure II.^{14,15} Since only one such product was detected,



it is likely that the Cr(V) species attacking N_2H_2 has the same ligand environment as that attacking N_2H_5^+ in the rate-determining sequence.

Reduction with Hydroxylamine.¹⁶ Hydroxylamine, NH_2OH , is isoelectronic with hydrazine, but aspects of its redox behavior are known to be quite different. Its reaction with Cr(V) chelate I (again in its bis(2-ethyl-2-hydroxybutyrate) modification) is smooth,

(13) It is reasonable to suspect that the two electrons transferred to Cr(V) are those constituting the Cr-N bond in precursor P and that the oxidized nitrogen species is thus free to depart after transfer despite the recognized substitution-inert character of Cr(III).

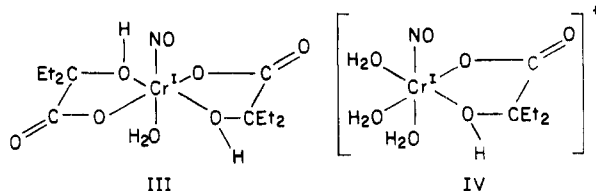
(14) Salts of aquo(carboxylato)chromium(III) ions are generally extremely water soluble and deliquescent and often undergo aquation in aqueous media within hours after this formation. They are therefore practically never isolated in pure form in mechanistic studies; their structures are instead inferred from their ion-exchange behavior and their electronic spectra.¹⁵

(15) For comparisons of spectra of chelated and nonchelated carboxylate complexes of chromium(III), see, for example: (a) Butler, R. D.; Taube, H. *J. Am. Chem. Soc.* 1965, 87, 5597. (b) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* 1964, 86, 1318. (c) Ward, J. R.; Haim, A. *J. Am. Chem. Soc.* 1970, 92, 475. (d) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* 1985, 24, 4679.

(16) Rajasekar, N.; Subramaniam, R.; Gould, E. S. *Inorg. Chem.* 1982, 21, 4110; 1983, 22, 971.

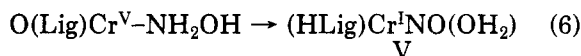
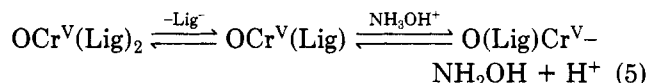
but here the stoichiometry is 1:1, implying that the net changes in oxidation states of the two reactants are equal in magnitude but in opposite directions. The reaction yields no detectable nitrogen-containing gas, for the nitrogenous product has become affixed to the reduced chromium center. Two yellow-brown products, one uncharged and the other a 1+ ion, are obtained; their ratio depends on the quantity of excess carboxylato ligand in the reaction mixture. Strong absorption near 440 nm, observed for both products, is not characteristic of Cr(III) complexes having O-donor ligands¹⁵ but has been reported by Ardon and Herman¹⁷ for the ion $\text{Cr}(\text{H}_2\text{O})_5\text{NO}^{2+}$.

Spectral and magnetic studies by Griffith¹⁸ have shown that Ardon's complex and several closely related species are $\text{N}\equiv\text{O}^+$ derivatives of the very unusual valence state Cr(I) rather than $\text{N}=\text{O}^-$ derivatives of Cr(III). The magnetic moment for Ardon's complex (which has one unpaired electron per chromium) is 2.2 μ_{B} ,¹⁸ that for $\text{Cr}(\text{ClO}_4)_3$ (three unpaired electrons) is 3.9 μ_{B} ,¹⁶ and that from the product of reduction of Cr(V) chelate I with N_2H_4 is 3.5 μ_{B} . The two products from the NH_2OH reaction exhibit moments of 2.3 and 2.6 μ_{B} , thus indicating the presence of only one unpaired electron per chromium¹⁹ and pointing to the conclusion that these, like Ardon's complex, are low-spin complexes of chromium(I) in which the metal center has the configuration $(t_{2g})^5$. This inference is confirmed by the appearance of strong IR absorbances at 1780 and 1860 cm^{-1} (very near the values reported for coordinated $\text{N}\equiv\text{O}^+$)¹⁸ but none near 1120 cm^{-1} (considered to be characteristic of coordinated $\text{N}=\text{O}^-$).²⁰ The low charges on the reaction products indicate that carboxylato ligation persists (as is the case for the reaction with N_2H_5^+), and the properties of these products are thus consistent with chelated structures III and IV.



Kinetic profiles of this reaction at several wavelengths (with NH_3OH^+ in excess) give no evidence for the intervention of a chromium(III) intermediate produced or destroyed on a time scale comparable to that for formation of Cr(I).

The rate law for this reaction,¹⁶ like that for the reduction by N_2H_5^+ , indicates the operation of a rapid equilibrium, involving loss of one ligand from the oxidant, prior to the redox act. The implication is the same—that the freed coordination position on Cr(V) is utilized by attachment to a donor site on the reductant:



(17) Ardon, M.; Herman, J. I. *J. Chem. Soc.* 1962, 507. These authors prepared this ion from NO and $\text{Cr}(\text{ClO}_4)_2$.

(18) Griffith, W. P. *J. Chem. Soc.* 1963, 3286.

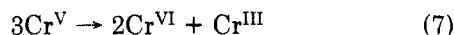
(19) Theoretical "spin only" magnetic moments are 1.7 μ_{B} for species with one unpaired electron and 3.9 μ_{B} for those with three unpaired electrons.

(20) Griffith, W. P.; Lewis, J.; Wilkinson, G. *J. Chem. Soc.* 1961, 775.

The two final products (assigned structures III and IV) appear to be formed via a competition between the ligand anion and solvent for the indicated intermediate V. As expected, the ratio of products, [III]/[IV], is proportional to $[\text{Lig}^-]$ in the reaction mixture.

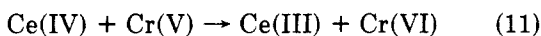
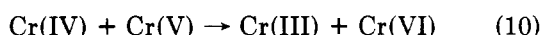
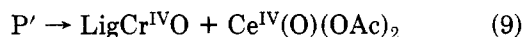
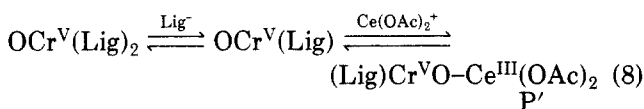
Thus, the reduction by hydroxylamine is initiated in the same way as that by hydrazine—with loss of one ligand per Cr(V) and formation of a $\text{Cr}^{\text{V}}\text{-N}$ precursor. The systems, however, diverge markedly after the initial act of electron transfer. The 2e oxidation of hydrazine yields N_2H_2 , which undergoes further rapid external oxidation to N_2 . In contrast, the $\text{Cr}^{\text{III}}\text{-N}^{\text{I}}$ species, arising (in principle) from a 2e transaction with hydroxylamine, quickly (perhaps instantaneously) undergoes a second internal 2e transfer, yielding the observed $\text{Cr}^{\text{I}}(\text{NO}^+)$ products. The occurrence of this unusual net change of 4e, in what appears to be a single transfer, may reflect, in large part, the strong mutual stabilization of the NO^+ group and the Cr^{I} center by strong metal-to-ligand back-bonding.^{21,22}

The Ce(III)-Catalyzed Disproportionation of Cr(V).²³ The disproportionation of carboxylato-bound chromium(V)



is promoted by polyvalent metal ions, by far the most effective of which is Ce^{3+} . Typically, reaction 7 for Cr(V) chelates of type I is accelerated three- to fivefold by La^{3+} , Pr^{3+} , Gd^{3+} , Tb^{3+} , and Al^{3+} (at the 0.08 M level) but greater than 10^2 -fold by 0.075 M Ce^{3+} . Significantly, Ce^{3+} differs from the other trivalent ions in the accessibility, in solution, of an oxidation state one unit higher. There is, however, no *net* conversion to Ce(IV) in the Ce(III)-catalyzed reaction.

The rate of disproportionation, as catalyzed by Ce(III) in acetate buffer, is, once again, proportional to $1/[\text{Lig}]$, indicating, in a third instance, rapid and reversible loss of carboxylato ligand from the oxidant prior to the rate-determining step. In addition, the overall reaction is second order in acetate. The activated complex thus includes one unit of the Cr(V) complex (from which one ligand has been removed), one unit of Ce(III), and two acetates (which are almost certainly associated with Ce^{III}). The proposed sequence, indicated below, features recycling of cerium between the tri- and quadrivalent states.



The final two steps, (10) and (11), are taken to be rapid parallel oxidations of Cr(V) with the two powerful oxidants, Cr(IV) and Ce(IV). Both are highly favored thermodynamically, and (11) has been shown independently to proceed much more rapidly than the

(21) See, for example: Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* **1966**, *7*, 277.

(22) For a more recent example of a 4e reduction, also involving hydroxylamine, see: Wieghardt, K.; Backes-Dahmann, G.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1983**, *22*, 1221.

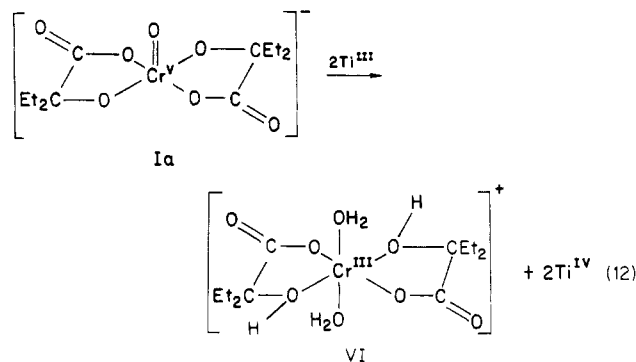
(23) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

catalyzed disproportionation under similar conditions.^{23,24}

The properties of the Cr(III) product conform to those of the nonchelated dipositive carboxylato complex $\text{R}_2\text{C}(\text{OH})\text{COOCr}(\text{H}_2\text{O})_5^{2+}$. The chelate ring in the Cr(V) reactant has thus undergone opening within the reaction sequence. It is most likely that this has occurred in the Cr(IV) state, for chelation is found to persist in those reductions^{12c,16} of carboxylato-bound Cr(V) which bypass Cr(IV). Moreover, earlier studies²⁵ indicate that ligand substitution at Cr(IV) is much more rapid than that at Cr(III), chelates of which are known to open sluggishly.^{15a}

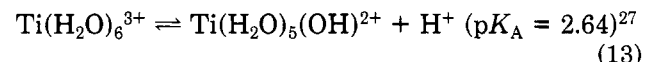
Reduction with Ti(III).²⁶ Tripositive titanium was the first of several single electron reductants examined in reaction with carboxylato-bound chromium(V). Such reactions necessarily pass through a Cr(IV) intermediate, and it was hoped that in favorable instances such an intermediate might be detected and its properties studied. As a group, these reductions are considerably more rapid than the reactions thus far considered, and measurements require stop-flow methods.

The stoichiometry of this reaction is, as expected, $2\text{Ti}(\text{III})/\text{Cr}(\text{V})$, but the Cr(III) product is found to be unipositively charged with a spectrum corresponding to that of a dichelate. The overall reaction may thus be represented



The primary Cr(III) species from this reaction is not the thermodynamically favored product, for it undergoes slow aquation, even in the presence of excess ligand. Although five stereoisomers (excluding enantiomorphs) may be envisaged for dichelates of type VI, the assigned structure is that most closely related to that of the Cr(V) reactant Ia.

The rate of this reaction is proportional to $1/[\text{H}^+]$, indicating a preliminary reversible loss of a proton from one of the reaction partners. The deprotonated active species is almost certainly $\text{Ti}(\text{OH})^{2+}$



in keeping with the redox behavior of the majority of Ti^{III} reductions that have been examined to data.²⁸

(24) Reaction 11 has been previously proposed as a rapid step in transformations in Ce-Cr systems by: (a) Doyle, M.; Swedo, R. J.; Roček, J. *J. Am. Chem. Soc.* **1973**, *95*, 8352. (b) Tong, J. Y.-P.; King, E. L. *J. Am. Chem. Soc.* **1960**, *82*, 3805.

(25) (a) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33. (b) Ogard, A. E.; Taube, H. *J. Phys. Chem.* **1958**, *62*, 357. Note that opening of the chelate ring is, in effect, in act of ligand substitution at the metal center. The "alcoholic" hydroxide is the leaving group whereas an additional water molecule is the entering group.

(26) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.

(27) Brunschwig, B. S.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1731.

Unlike the reductions by hydrazine and hydroxylamine, reaction with Ti(III) is not retarded by excess carboxylato ligand nor by its parent acid. Instead it is accelerated, not only by the ligand but also by other α -hydroxy acids and their anions. Thus, dissociation of chelating ligand prior to formation of a precursor complex is not necessary here. The acceleration by added α -hydroxycarboxyl species is doubtless associated with partial conversion of $\text{Ti}(\text{OH})^{2+}$ to a carboxylato-bound complex, a conversion for which there is independent spectral evidence.²⁶ Earlier work²⁹ has demonstrated that incorporation of a carboxyl group at a Ti(III) center results in marked increases in redox rates, irrespective of reaction mechanism.³⁰

The bimolecular specific rate for reduction of chelate Ia by $\text{Ti}(\text{OH})^{2+}$ is $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (23 °C, $\mu = 0.5 \text{ M}$). This is considerably greater than $10^4 \text{ M}^{-1} \text{ s}^{-1}$, the estimated^{28d,31} substitution-controlled limit for inner-sphere reactions at a Ti(III) center. This difference may be taken as strong evidence that this reaction is predominantly outer sphere.

In principle, the intermediate oxidation state Cr(IV) must intervene in this reaction. Although this state appeared in subsequent work (see below) as a strongly absorbing species in the medium at hand, kinetic profiles of the Ti(III) reaction failed to detect such a transient in this instance, indicating that the Cr(IV) intermediate reacts with the reductant much more rapidly than does the Cr(V) chelate taken as the original reactant. Specifically, it may be estimated²⁶ that the ratio of two rates must exceed 20 in order that the faster kinetic component go undetected. The specific rate for reaction of $\text{Ti}(\text{OH})^{2+}$ with Cr(IV) then exceeds $1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, clearly too rapid for an inner-sphere process involving this reductant.

If structure VI assigned to the Cr(III) product is correct, the composite electron-transfer sequence ($\text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}}$) has proceeded with preservation of the ligand connectivity about chromium, implying that ligand substitution about Cr(IV) is slower than the reaction of that intermediate with Ti(III) and that the Cr(IV) transient is a bis(chelate), probably with an additional oxo ligand (in analogy with the pentavalent structure of V(IV) in solution). The Ti(III) reduction contrasts with the Ce(III)-catalyzed disproportionation, in which modification of the ligand environment at Cr(IV) (chelate ring opening) appears to occur. This difference in behavior is not unreasonable, for such inner-sphere alteration is competing with reduction of Cr(IV), and reduction is undoubtedly much more rapid with strongly reducing Ti(III) than with weakly reducing Cr(V).

(28) See, for example: (a) Earley, J. E.; Bose, R. N.; Berrie, B. H. *Inorg. Chem.* **1983**, *22*, 1836. (b) Hery, M.; Wieghardt, K. *Inorg. Chem.* **1978**, *17*, 1130. (c) Thompson, G. A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 638. (d) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103.

(29) (a) Thompson, G. A. K.; Sykes, A. G. *Inorg. Chem.* **1979**, *18*, 2025; (b) Lee, R. A.; Earley, J. E. *Inorg. Chem.* **1981**, *20*, 1739.

(30) For inner-sphere reactions, these rate enhancements have been attributed to labilization of Ti(III)-bound water molecules (by carboxyl coligands) prior to formation of a precursor.^{29b} For outer-sphere reactions, accelerations are more modest and their origin less obvious.

(31) Diebler, H. Z. *Phys. Chem. (Frankfurt am Main)* **1969**, *68*, 64. This author reports a unimolecular rate constant $8 \times 10^5 \text{ s}^{-1}$ for substitution of NCS^- in the ion pair $\text{Ti}(\text{H}_2\text{O})_6^{3+}$, NCS^- (9 °C). This value, in conjunction with the estimated formation constant for this ion pair (1 M^{-1}), leads to a bimolecular specific rate near $8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the composite process.

Reductions by Fe^{2+} and by VO^{2+} . Detection of Cr(IV).^{15d,32} Reductions of Cr(V) chelate I ($R_1 = R_2 = \text{Et}$) with Fe(II) and with VO^{2+} are similar, in some respects to that with Ti(III). The stoichiometry of the reactions, with reductant (Red^{2+}) in excess, is cleanly $2\text{Red}^{2+}/\text{Cr}(\text{V})$, the Cr(III) product from both reductions is again a unipositive bis(chelate), and neither reaction is inhibited by excess ligand anion, thus ruling out predissociation of the ligand from the Cr(V) reactant prior to electron transfer. A prominent difference is the observed intervention of the Cr(IV) intermediate in the Fe^{2+} and VO^{2+} reductions. In solutions of pH 2–4, in which $[\text{Lig}^-] = 10^{-4}$ – 10^{-2} M , this intermediate makes its appearance as a strongly absorbing species ($\lambda_{\text{max}} 515 \text{ nm}$ ($\epsilon 1.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)).³³ The intervention of this intermediate in both reactions, and in reduction by U(IV) as well,³⁴ the ease with which it is consumed by 1e reductants in excess, and the observation that it is ESR silent at room temperature³⁵ support the assigned oxidation state, as does the ESR-monitored titration of Cr(V) with VO^{2+} .³⁶

With either Fe^{2+} or VO^{2+} in excess, the growth of this intermediate and its rapid reduction may be observed, whereas with Cr(V) in excess, only its growth is seen, after which slow disappearance, by a combination of disproportionation and ligand oxidation, is apparent. The rate law for generation of the intermediate with Fe(II)³² points to two paths for the conversion of Cr(V) to Cr(IV). The first of these passes through a transition state consisting of Fe(II) and Cr(V) with one proton removed (probably from the "alkoxyl" oxygen of the chelate),³⁷ whereas the second proceeds through an activated complex of composition $\text{Cr}(\text{V}) + \text{Fe}(\text{II}) + \text{Lig}^-$. The latter path is taken to represent reduction of the Cr(V) chelate by the complex FeLig^+ , the rate enhancing action by carboxylato ligation of the reductant being presumably analogous to that observed in Cr(V)–Ti(III) systems. Reduction of the Cr(IV) intermediate by excess Fe(II) proceeds at a specific rate $2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (21 °C, $\mu = 0.50 \text{ M}$) and is independent of acidity and ligand concentration in the range examined (pH 2–4, $[\text{Lig}^-] = 0.001$ – 0.030 M).

The kinetic profiles for the reaction of Cr(V) with excess VO^{2+} are rather more complicated, for in addition to the rapid growth and decay of the Cr(IV) intermediate, a third (minor) kinetic component is detected.^{15d} The rate law for the rapid formation of Cr(IV) is consistent with an activated complex formed from one unit each of Cr(V) and V(IV) with additional

(32) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.

(33) This intermediate appears to persist only in the presence of excess Cr(V), which absorbs strongly in the ultraviolet. Reflecting this constraint, useful UV spectra of the Cr(IV) intermediate have not yet been obtained, even by difference. Stabilization evidently requires a large excess of chelating ligand as well; at lower values of $[\text{Lig}^-]$, the two oxidation states react, yielding Cr(III) and Cr(VI) (eq 10).

(34) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 94.

(35) Chisholm, and co-workers^{11d} report alkoxide complexes of Cr(IV) to be ESR silent at temperatures above 98 K.

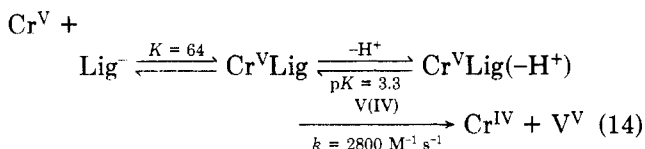
(36) Specifically, the addition of 0.1–0.3 equiv of VO^{2+} to 1 equiv of Cr(V) reduces the intensity of the Cr(V) ESR signal to a value indicating the consumption of just one Cr(V) per added VO^{2+} .^{15d} However, at higher ratios of V(IV) to Cr(V), departures from this 1:1 stoichiometry become increasingly pronounced, reflecting the competing reaction of Cr(IV) with V(IV). When 2 equiv of V(IV) have been added, the 8-line VO^{2+} signal appears, confirming the 2:1 stoichiometry which obtains with excess V(IV).

(37) A reaction of $\text{Fe}(\text{OH})^+$ with the Cr(V) dichelate is also compatible with the kinetic description of the deprotonated path but would require a bimolecular rate constant near $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is comparable to the diffusion-controlled limit for reactions of this type in solution.

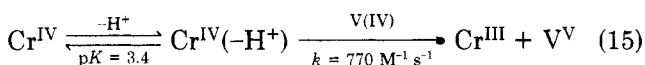
unit of carboxylato ligand and loss of one H⁺. Both the ligation ($K = 64 \text{ M}^{-1}$) and the deprotonation ($\text{p}K_{\text{A}} = 3.3$) exhibit kinetic saturation in the concentration range studied, and both processes are taken to pertain to the Cr(V) oxidant.³⁸ The rate law for the rapid reduction of Cr(IV) suggests a transition state having one unit each of Cr(IV) and V(IV), formed with loss of a proton (acidity constant $4 \times 10^{-4} \text{ M}^{-1}$, a value which agrees with that for the Cr(IV) intermediate, determined independently).

The principal sequence in the overall conversion of Cr(V) to Cr(III) may then be represented schematically as follows (only the kinetically active ligand, Lig⁻, is included):

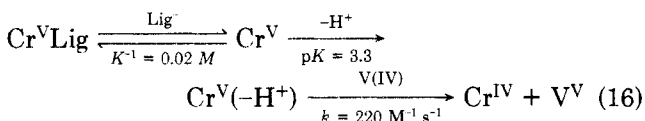
Conversion to Cr(IV)



Reduction of Cr(IV)



The third (slow) component appears to pertain to reduction of the Cr(V) chelate (without the extra ligand), activated again by loss of a proton (once more, only the kinetically active ligand is indicated):



Appearance of this as a separate kinetic component requires that the equilibrium between Cr(V) species be established slowly in comparison to the reductions, a conclusion in accord with a more recent study of alteration of the ligand environment about this metal ion center.^{3a,39}

In the reduction by Ti(III), reaction with Cr(V) was found to be less than 1/20th as rapid as that with Cr(IV), both steps proceeding mainly by outer-sphere paths. With reductions by Fe(II) and VO²⁺, specific rates for the analogous steps lie much closer to each other, and in the case of the principal VO²⁺ reduction sequence, Cr(V) reacts somewhat more rapidly than Cr(IV). A corollary of the Marcus model for outer-sphere reactions^{40,41} is that the ratio of specific rates pertaining to a pair of 1e oxidants should be the same for all outer-sphere reductants. Substantial departures from this ratio are indicative of the operation of an additional route (i.e., an inner-sphere path). The alteration in rate ratios is then in the direction pointing to predominant inner-sphere paths for the Cr(V)-Fe(II) and Cr(V)-VO²⁺ reactions. No such conclusion can be drawn for the corresponding reductions of Cr(IV).

(38) Independent spectrophotometric evidence for "extraligation" of the Cr(V) chelate in the media studied has been obtained.^{15d} The observed association constant is 51 M^{-1} .

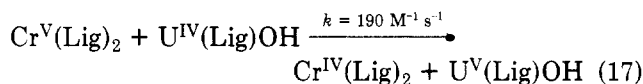
(39) Two different intermediate Cr(IV) species are expected to form initially if the ligand environments correspond to those of their Cr(V) precursors as represented in sequences (14) and (16). A single kinetic component observed for reduction of Cr(IV) indicates that the ligand-exchange reaction involving Cr(IV) is faster than reduction to form the Cr(III) product.

(40) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853.

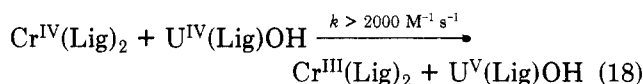
(41) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

Reductions with Uranium(IV).³⁴ As a consequence of the recognized stability of hexapositive uranium (as UO₂²⁺), U(IV) is generally taken to be a 2e reductant. However, uranium(V) is known to intervene in certain reductions of UO₂²⁺,⁴² allowing us to consider the possibility that the Cr(V)-U(IV) reaction may proceed, at least in part, by 1e steps and that the two unusual states U(V) and Cr(IV) may coexist in solution.

Reduction of Cr(V) bis(chelate) I ($R_1 = R_2 = \text{Et}$) with U(IV) proceeds with 1:1 stoichiometry, yielding the same Cr(III) chelate VI obtained with the 1e metal ion reductants. With U(IV) in excess, the Cr(IV) intermediate is again observed, but distortion of the kinetic profiles due to its intervention is much less pronounced than in the Fe(II) and VO²⁺ reactions, indicating that the component steps in the reduction sequence have quite different rates. The rate law for growth of the Cr(IV) intermediate⁴³ is consistent with a transition state formed from the Cr(V) chelate and a uranium(IV) species that has taken on an extra ligand but lost a proton ($\text{p}K_{\text{A}} = 2.4$), designated U^{IV}(Lig)OH:



This is followed by rapid reduction of the Cr(IV) intermediate by a second unit of quadrapositive uranium



The fate of the U(V) intermediate in this reaction has not yet been established, but bimolecular disproportionation ($2\text{U}^{\text{V}} \rightarrow \text{U}^{\text{IV}} + \text{U}^{\text{VI}}$) is in accord with the observed stoichiometry.

The ratio of specific rates $k_{\text{Cr(IV)}}/k_{\text{Cr(V)}}$ in this system exceeds 10; it thus resembles that in the Cr(V)-TiOH²⁺ system and is consistent with assignment (although with reservations)⁴⁵ of an outer-space path for the U(IV) reaction. This appears to be the first instance in which U(V) is prepared by oxidation, rather than by reduction.

Reduction with Sulfite.⁴⁶ The reduction of chromium(V) with SO₃²⁻ was expected to be a straightforward bimolecular reaction between a pair of 2e redox species. It was not. With SO₃²⁻ in excess, the rate of which Cr(V) chelate ($R_1 = R_2 = \text{Et}$) was consumed in a kinetic run did not decrease in the usual fashion to generate the anticipated exponential curve. Instead variation in slope was slight, and in many experiments rate increases were observed, indicating autocatalysis.

(42) See, for example: (a) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1965**, *4*, 1166. (b) Mastragostino, M.; Saveant, J.-M. *Electrochim. Acta*, **1968**, *13*, 751. (c) Ekstrom, A. *Inorg. Chem.* **1973**, *12*, 2455; **1974**, *13*, 2237.

(43) An ambiguity arises in assignment of rate constants to the two components in the biphasic curves obtained, not only in the reduction by U(IV) but also in those by Fe(II) and VO²⁺ (see, for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; Chapter 4). In each case the ambiguity is resolved by assigning values that lead to a calculated extinction coefficient of the Cr(IV) intermediate in agreement with that obtained from experiments with Cr(V) in excess.

(44) Rate constants for the Cr(IV)-U(IV) reaction may be evaluated in particular systems, but since they are obtained from relatively small departures from simple exponential behavior, they must be considered highly approximate. The active reducing species in (18) is represented as a hydroxy complex to reflect the retardation of this process by increases in [H⁺]. Since the precise form of the acidity dependence for this step has not been evaluated, the limiting specific rate is given only as a lower limit.

(45) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

(46) Bose, R. N.; Srinivasan, V. S.; Rajasekar, N., unpublished experiments, Kent State University, 1982-1985.

Table I.
Mechanistic Features of Reductions of Chelated Chromium(V) with Inorganic Reducing Agents^a

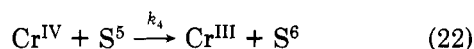
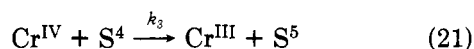
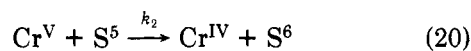
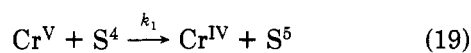
reductant	<i>n</i> ^b	IS or OS?	predominant reactive oxidizing species	predominant reactive reducing species	ref
N ₂ H ₅ ⁺	2	IS	Cr ^V O(Lig)(-H ⁺)	N ₂ H ₅ ⁺ , ^c N ₂ H ₂	12c
NH ₃ OH ⁺	4 ^d	IS	Cr ^V O(Lig)(-H ⁺)	NH ₃ OH ⁺ ^c	16
Ce(III) ^e	1	IS	Cr ^V O(Lig)(-H ⁺)	Ce(OAc) ₂ ⁺ ^c	23
Ti(III)	1	OS	Cr ^V O(Lig) ₂ ⁻	TiOH ²⁺ and Ti(Lig)OH ⁺	26
Fe(II)	1	IS	Cr ^V O(Lig) ₂ (-H ⁺) ²⁻	Fe ²⁺ and Fe(Lig) ⁺	32
V(IV)	1	IS	Cr ^V O(Lig) ₃ ²⁻	VO ²⁺ and VO(Lig) ⁺	15d
U(IV)	1	OS	Cr ^V O(Lig) ₂ ⁻	U ^{IV} (Lig)(OH) ²⁺	34
S(IV)	1 ^f	both	Cr ^V O(Lig)(-H ⁺)	HSO ₃ ⁻	46

^aReactions of Cr(V) chelate I (R₁ = R₂ = Et) in aqueous media pH 2-4. (Lig⁻) = 2-ethyl-2-hydroxybutyrate. ^bNumber of electrons involved in the initial electron transfer. ^cPrecursor complex formed with loss of one H⁺. ^dPrincipal product was Cr^I(NO⁺). ^eCe(III) catalysis of the disproportionation of Cr(V) to Cr(III) and Cr(VI). ^fAutocatalytic reaction; catalytic species is Cr(IV).

However, the spent reaction mixture (containing Cr^{III} and SO₄²⁻) exhibited no catalytic activity. In addition a small but sudden drop in absorbance appeared near the end of the reaction, and this feature could be made much more prominent by monitoring the reaction at a wavelength where the Cr(V) reactant and the final Cr(III) product have very nearly equal molar absorptivities (Figure 1). The discontinuity at 426 s in curve A, at which point little, if any, Cr(V) remains, suggests that an absorbing intermediate species is suddenly consumed by a reaction which is inhibited by Cr(V) when present.

These most unusual kinetic profiles can be rationalized only by assuming that neither of the primary reagents undergoes a simple 2e conversion to the final product but that SO₃²⁻ is initially converted to the SO₃⁻ radical anion (abbreviated S⁵) and that the conversion of Cr^V to Cr^{III} must again pass through Cr^{IV}, which is the predominant absorbing species in curve A. Furthermore, the shapes of the curves demand that Cr^V reacts much more rapidly with radical S⁵ than does Cr^{IV} (being, in effect, a scavenger for S⁵).

Four reactions (each a 1e transaction) contributing to the overall conversion are indicated (only the oxidation states are designated):



At the beginning, only (19) and (20) occur, but as Cr^{IV} accumulates, (21) assumes importance, yielding an increased concentration of S⁵. The latter reacts more rapidly with Cr^V than with Cr^{IV}, but reaction with Cr^V regenerates Cr^{IV} via (20) (hence the autocatalysis). When Cr^V is exhausted, only (21) and (22) take place, resulting in the nearly pseudo-first-order loss of Cr^{IV}. When the steady-state approximation is applied to S⁵, sequence (19)–(22) reproduces curves A and B, if *k*₁ is taken as 0.023 M⁻¹ s⁻¹, *k*₃ as 3.1 M⁻¹ s⁻¹, and the ratio *k*₂/*k*₄ is taken as 30, along with extinction coefficients of the three oxidation states of chromium (at the two wavelengths, 600 and 355 nm) determined independently.

Note that the ratio of reactivities of Cr(V) and Cr(IV) toward SO₃²⁻ (*k*₁/*k*₃) is 0.006 in the medium used. This ratio is consistent with an outer-sphere mechanism for

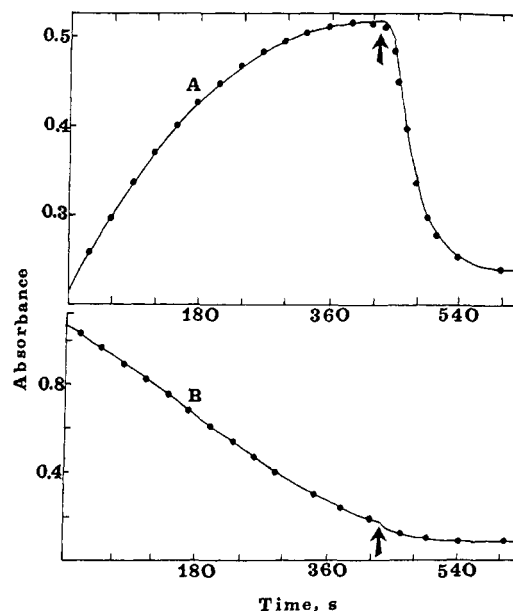


Figure 1. Kinetic profiles at 600 nm (curve A) and 355 nm (curve B) for reaction of Cr(V) chelate I (1.10 × 10⁻³ M) with sulfite (9.68 × 10⁻³ M) at 21 °C. The supporting medium was 0.05 M each in 2-ethyl-2-hydroxybutyric acid and its sodium salt (pH 3.4); μ = 0.5 M (NaClO₄). Optical path lengths were 5.00 cm for curve A and 1.00 cm for curve B. Note the sharp "break point" in curve A at 426 s. The principal absorbing species is Cr(IV) in curve A and Cr(V) in curve B. The solid lines are experimental curves, whereas the small circles represent absorbance changes calculated from sequence (19)–(22) in the text, taking *k*₁ and *k*₃ as 0.023 and 3.1 M⁻¹ s⁻¹ and the ratio *k*₂/*k*₄ as 30.

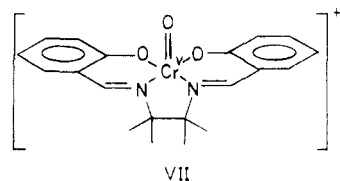
both (19) and (21) but does not demand this.⁴⁵ The corresponding ratio for reaction with SO₃⁻ (*k*₂/*k*₄ = 30) points to an inner-sphere path for the Cr^V-S⁵ reaction, (20).

Concluding Remarks. Table I summarizes the characteristics of the reductions of carboxylato-bound chromium(V) thus far examined. Among the eight entries, we see considerable variation with respect to mechanism, to the number of electrons accepted in the initial transfer, and to selectivity among ligation and protonation levels of the Cr(V) oxidant. As additional reductants are examined, further mechanistic diversity is to be expected, and initial studies⁴⁷ of reductions with Mn(II) and S₂O₄²⁻ suggest the fulfillment of this expectation.

A glance at areas other than those with which this author has been directly involved serves to emphasize

(47) Fanchiang, Y.-T.; Bose, R. N., unpublished experiments, 1984–1985.

the breadth of interest surrounding a metal oxidation state which is thought, by a substantial fraction of practicing chemists, not to occur. For example, although chelates of type I have thus far proved disappointing as regiospecific oxidants for alcohols, glycols, and hydroxy acids,^{3a} the Cr^{VO} Schiff's base complex VII



has been found^{3b,48} to oxidize olefins (to epoxides) and phosphines (to phosphine oxides) smoothly under unusually mild conditions. In addition, Cr(V) complexes constitute a fertile area for theoretically inclined workers, who have sought to reconcile the electronic

(48) Siddall, T. L.; Miyaura, N.; Huffman, J. C.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1185. Complex VII is readily prepared by oxidation of the corresponding Cr(III) chelate with iodosobenzene, C₆H₅IO. Oxidations with VII can be incorporated into a catalytic cycle by using catalytic quantities of the Cr(III) precursor with stoichiometric amounts of iodosobenzene and the organic reductant.

spectra,^{4a,49} detailed ESR spectra,⁵⁰ and magnetic properties^{4b} of such compounds with orbital occupancy and ligand environment. Finally, preliminary evidence⁵ has been presented implicating Cr(V) species as carcinogens in a number of biosystems featuring interactions of ribonucleotides with added chromate.

Even more widespread attention to this unusual oxidation state is anticipated as additional investigators become aware of the ease with which it is obtained.

It is a pleasure to acknowledge the contributions of Drs. V. S. Srinivasan, N. Rajasekar, Y.-T. Fanchiang, and R. N. Bose, who carried out the work upon which a major portion of this Account is based. I am also indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for continued support of this research.

(49) See, for example: (a) Gray, H. B.; Hare, C. R. *Inorg. Chem.* **1962**, *1*, 363. (b) Milstein, J. B.; Ackerman, J.; Holt, S. L.; McGarvey, *Inorg. Chem.* **1972**, *11*, 1178.

(50) (a) Hare, C. R.; Bernal, I.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 831. (b) Greenblatt, M.; Pifer, J. H.; Banks, E. J. *J. Chem. Phys.* **1977**, *66*, 559. (c) Ziebarth, O. V.; Selbin, J. J. *Inorg. Nucl. Chem.* **1970**, *32*, 849. (d) Dalton, L. A.; Bereman, R. D.; Brubaker, C. H., Jr. *Inorg. Chem.* **1969**, *8*, 2477. (e) Garner, C. D.; Hillier, I. H.; Mabbs, F. E.; Taylor, C.; Guest, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2258.

Small, Strained Bicycloalkyl Radicals and Some Homolytic Reactions Involving Their Parent Bicycloalkanes¹

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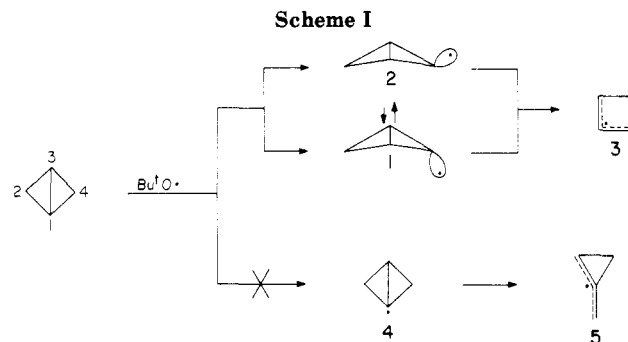
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Chemical species containing small, strained bicycloalkyl structures are interesting because the rigid framework of carbon atoms can lead to unusual and even unprecedented chemical behavior. The presence of a large amount of strain energy makes C-C bond scission a common process. Study of the regioselectivity and kinetics of homolytic decompositions and rearrangements of bicycloalkanes and bicycloalkyl radicals helps the organic chemist to understand how molecules behave when pushed toward the limits of stability. It also provides valuable data for the evaluation and calibration of the results of theoretical calculations. Additional benefits result from the discovery of novel transformations and procedures with synthetic potential.

Electron paramagnetic resonance (EPR) spectroscopy is a particularly useful technique for confirming the existence of various strained radicals that seem likely to be reaction intermediates.² It is also an ideal tech-

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nique for revealing the distribution of spin density in radicals and hence the nature of the semioccupied molecular orbital (SOMO) and the radical's configuration and conformation.² Much of this account is therefore devoted to our EPR studies of bicycloalkyl radicals.

Hydrogen Atom Abstraction from Bicycloalkanes

Bicyclo[*n*.1.0]alkanes. The simplest radical from this class of hydrocarbons, bicyclo[1.1.0]but-2-yl (1), was also the first to be studied. Krusic et al.³ generated this

(1) Issued as NRCC, No. 25430.

(2) J. K. Kochi, *Adv. Free Radical Chem.*, **5**, 189 (1975).