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Redox chemistry of chromium(IV) complexes

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ABSTRACT

A short introduction summarizes scattered preparations of chromium(V) and chromium(IV) derivatives before 1975 and places these unusual states in perspective with respect to the more usual oxidation states of this element. Preparations of peroxo complexes of Cr(IV), known since the turn of the century, are described and their redox reactions, as investigated since 1988, are treated. Systems in which Cr(IV) has been detected in the course of reductions of water-soluble Cr(V) complexes are enumerated and the role of Cr(IV) in some autocatalytic systems and "clock reactions" is considered. The stabilization of Cr(IV) via chelation with the anions of α-hydroxy acids is described and the reactions of this type of chelate are discussed. The recent preparations of aqua-substituted Cr(IV) are mentioned and the role of the $2e^-$ change Cr(IV)→Cr(II) in the oxidations of organic substrates by Cr(VI) is indicated. Finally, experimental values for the standard potential and electron self-exchange rate for the Cr(III/IV) couple are compared with the corresponding parameters for Cr(IV/V) in a similar medium and structural implications are drawn from these rates.

1. INTRODUCTION

Until the mid 1970s the known aqueous chemistry of chromium dealt almost exclusively with the oxidation states +6, +3 and +2. Interconversions between the first two of these had been carried out since the early 19th century, while Cr(II) had

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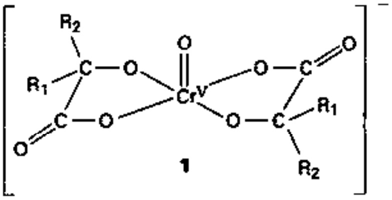
achieved prominence in the 1950s through Taube and co-workers' experiments which did much to unravel the mechanisms of electron transfer in solution [1].

As early as 1949 Watanabe and Westheimer [2] described kinetic experiments which appeared to indicate the intervention of the less usual states Cr(IV) and Cr(V) in the oxidation of 2-propanol with CrO_3, and during the 1960s evidence was being compiled that both of these "hypervalent" states were intermediates when CrO_4^{2-} or $Cr_2O_7^{2-}$ was reduced with such $1e^-$ reagents as Fe(II), V(IV) and Cr(II) (see e.g. refs. 3a–d; for a critical review see ref. 3e).

Recent interest in the chemistry of Cr(V) has been bolstered by the success in synthesizing compounds of this state. Over three dozen Cr(V) derivatives, ranging in complexity from CrF_5 [4] to porphyrin complexes [5], have now been characterized. Especially notable is a group of bis(chelates) with structures of type **1**, first prepared in 1978 by Krumpolc and co-workers by the action of CrO_3 on α-hydroxy carboxylic acids [6]. These complexes dissolve in aqueous media, yielding solutions in which the Cr(V) center is retained. The ready availability and stability of such Cr(V) derivatives make them attractive candidates for mechanistic examinations of the reactions of this state, and a host of studies pertaining to the redox chemistry of Cr(V) were described between 1981 and the present. For such investigations the bis(2-ethyl-2-hydroxybutyrato) complex (**1**; $R_1 \equiv R_2 \equiv C_2H_5$), the most stable of these chelates, has generally been the oxidant of choice. Early reviews of Cr(V) chemistry appeared in 1985 [7] and 1986 [8] and a more detailed treatment in 1992 [9]. Interest has been further enhanced by evidence implicating Cr(V) species as carcinogens in biosystems featuring interactions of ribonucleotides with added chromate (see e.g. ref. 10).



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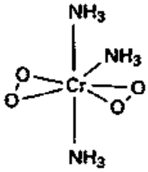
The present review deals with the chemistry of tetrapositive chromium, Cr(IV), a state which may be considered even less characteristic than Cr(V). Scattered reports of preparations of Cr(IV) compounds appeared before 1975 (see e.g. ref. 11), but these species generally underwent disproportionation (to Cr(III) and Cr(VI)) in aqueous media. More recently oxochromium(IV) ($Cr^{IV}O$) derivatives of an array of porphyrins have been described [12], but again these generally do not survive long enough in water to allow the chemistry of this state in solution to be readily examined. In 1991 Scott et al. [13] reported preparations in solution of an unusually simple Cr(IV) species exhibiting behavior corresponding to the oxo cation $[Cr^{IV}O]^{2+}$ (aq), which was found to decay in aqueous solution with a half-life of 30 s at room temperature.

In line with the author's interest in aqueous chemistry, emphasis will be on Cr(IV) species which are sufficiently stabilized in water by ligation to allow observations of their reactions using conventional techniques.

2. PEROXO COMPLEXES

Although much of the chemistry of Cr(IV) has been developed recently, one aspect dates back to the turn of the century. Treatment of CrO_3 (in the cold) with an aqueous solution of a nitrogenous base (including CN^- or ammonia) and concentrated H_2O_2 yields a group of olive-green chromium(IV) diperoxo ammines. Prototype members of this series featured ligated ammonia [14] and ethanediamine [15]. Aqueous solutions of these complexes are stable for several hours between pH 2 and 6, but the crystalline solids occasionally explode when dry and are best handled using plastic utensils and in quantities less than 500 mg [16].

Crystallographic studies [17] show that the metal center in these complexes is typically bound to three nitrogen and four oxygen atoms, forming a pentagonal bipyramid (2), and is in that sense seven coordinate. The oxidation state of chromium in such derivatives may be established by measurements of magnetic susceptibility (two unpaired electrons per Cr atom) [16,17] and confirmed iodometrically (five oxidizing equivalents per Cr atom). A particularly robust complex of this type, 3, is derived from the tridentate base diethylenetriamine ($NH_2(CH_2)_2NH(CH_2)_2NH_2$ ≡ "dien") [18].



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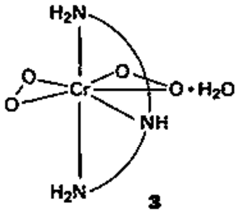


3

Although long known, diperoxochromium(VI) complexes attracted little attention, and indeed a number of their decomposition reactions in mineral acid, giving, as expected, Cr(VI), Cr(III) and O_2 (see e.g. ref. 19), appear to be relatively unexciting. However, one behavioral feature is notable: when reductions or decompositions are carried out in the presence of anionic ligands (e.g. halides or carboxylates), there is an impressive degree of rapid incorporation of these ligands in the Cr(III) product, despite the proverbial substitution-inert character of that metal center. Thus Garner and coworkers [20] adapted a method first described by Werner [21], in which polyhalo-substituted chromium(III) complexes were prepared by decomposition of diperoxochromium(IV) species in HF, HCl or HBr. The following conversions are typical:

$$\mathrm{Cr^{IV}(dien)\,(O_2)_2 \xrightarrow{\text{conc. HCl}} Cr^{III}(dien)\,Cl_3}$$

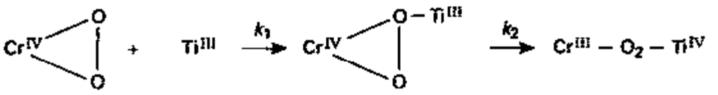
$$\mathrm{Cr^{IV}(en)\,(O_2)_2(OH_2) \xrightarrow{HF+NH_4HF} NH_4[Cr^{III}(en)F_4]}$$

$$\mathrm{Cr^{IV}(en)\,(O_2)_2(OH_2) \xrightarrow{\text{conc. HBr}} [Cr^{III}(en)\,(OH_2)_2Br_2]Br}$$

Although a number of the Cr(III) products so obtained are difficultly accessible, the synthetic applicability of conversions of this type appears to be limited, because in most instances two or more Cr(III) complexes are formed. Separation of such products using ion exchange chromatography is often tedious and generally attended by partial aquation of the halo substituents [20c].

On the other hand, such diperoxochromium(IV) complexes are attractive candidates for mechanistic studies since they feature two different strongly oxidizing functions in the same molecule. Initial redox studies with the diethylenetriamine (dien) derivative 3 suggested considerable versatility of action [16]. Aqueous solutions of this complex in glycine or acetate buffers react rapidly with VO^{2+}, $Fe(CN)_6^{4-}$ and Ti(III). With VO^{2+} the Cr(IV) center, but not the peroxo ligands, is reduced, while $Fe(CN)_6^{4-}$ and Ti(III) reduce both functions. The Cr(III) products contain bound "dien", and during the course of reaction with Ti(III), carboxylate groups from the buffer system also enter the coordination sphere of chromium. Rate laws for reduction by $Fe(CN)_6^{4-}$ and VO^{2+} feature prominent $[H^+]$-proportional terms, indicating involvement of a protonated form of the peroxo complex for which pK_A is less than 0.5. Reductions with Ti(III) appear to proceed through a strongly absorbing intermediate ($\varepsilon_{380} = 600\ M^{-1}\,cm^{-1}$) which decays unimolecularly ($k = 0.20\ s^{-1}$ at 25°C); the behavior of this species corresponds to that of a Cr^{IV}–Ti^{III} precursor complex formed prior to the act of internal electron transfer.

The ease with which external anions enter the coordination sphere of the Cr(III) product deserves comment, since such carboxylate incorporation at the $Cr^{IV}(O_2)_2$ center has been shown to be very slow in the absence of redox, and ligand exchange in Cr(III) centers is even more sluggish. Observations on the $Cr^{IV}(O_2)_2$–Ti^{III} reaction appear to be consistent with the sequence (1)–(5), in which formation of the precursor ($k_1 = 6 \times 10^3\ M^{-1}\,s^{-1}$) and its decay ($k_2 = 0.2\ s^{-1}$) generate the observed kinetic profiles:



(1)

$$\mathrm{Cr^{III}{-}O_2{-}Ti^{IV}} \xrightarrow{\mathrm{H_2O}} \mathrm{Cr^{III}{-}O_2H + Ti^{IV}OH} \tag{2}$$

$$\mathrm{Cr^{III}{-}O_2H + Ti^{III} \rightarrow Cr^{III}{-}O^{\cdot} + Ti^{IV}OH} \tag{3}$$

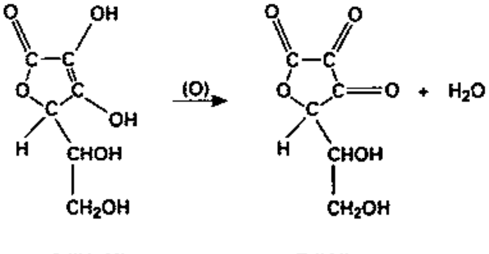
$$\mathrm{Cr^{III}{-}O^{\cdot}} \xrightarrow{\mathrm{H^+}} \mathrm{Cr^{IV}{-}OH} \xrightarrow{\mathrm{Lig}} \mathrm{Cr^{IV}{-}Lig} \tag{4}$$

$$\mathrm{Cr^{IV}{-}Lig + Ti^{III} \rightarrow Cr^{III}{-}Lig + Ti^{IV}} \tag{5}$$

The initial act of electron transfer (eqn. (1)) is almost certainly accompanied by breakage of a chromium–peroxy bond as seven-coordinate Cr(IV) is converted to six-coordinate Cr(III). The proposed Cr(III)–peroxy intermediate brings to mind related complexes described by Adams et al. [22], who emphasized the ease with which such complexes decompose in aqueous media. It is reasonable that subsequent attack by Ti(III) on the hydroperoxo complex results in homolysis of the O–O bond (eqn. (3)), that the resulting $\mathrm{Cr^{III}{-}O^{\cdot}}$ fragment is rapidly converted via internal electron transfer to a $\mathrm{Cr^{IV}{-}O}$ complex (eqn. (4)) and that the rapid ligand exchange involves the latter oxidation state, which, like its isoelectronic counterpart V(III), would be expected to be substitution labile in the absence of strongly chelating groups (see e.g. ref. 23). The suggested $\mathrm{Cr^{IV}{-}OH}$ species in (4) is closely related to the protonated form of aquachromium(IV) (Section 6). We cannot say whether the indicated conversion of $\mathrm{Cr^{III}{-}O^{\cdot}}$ to $\mathrm{Cr^{IV}{-}OH}$ occurs instantaneously or whether there is a delay attributable to a multiplicity difference between the two species. Note that reduction by $\mathrm{VO^{2+}}$, during which O–O bonds remain unbroken, is not accompanied by intrusion of external carboxylate groups.

Peroxochromium(IV) complexes react much more sluggishly with organic reductants, but certain of these reactions are strikingly accelerated by traces of transition metal ions. The oxidation of ascorbic acid (**4**) to dehydroascorbic acid (**5**) using the dien complex **3** has been examined in some detail [24,25]. The overall conversion of **4** to **5** is a net $2e^-$ change but often proceeds in single-electron steps, with the initial conversion of $\mathrm{H_2A}$ to the hydroascorbate radical $\mathrm{HA^{\cdot}}$ being the rate-determining step (see e.g. ref. 26).

The very slow $\mathrm{Cr^{IV}(O_2)_2}$–ascorbate reaction in acetate buffer is markedly



4 ('$\mathrm{H_2A}$') **5** ('A')

catalyzed by Fe(II), Fe(III), Cu(II) and VO^{2+}. Addition of an excess of the sequestrant EDTA strongly inhibits catalysis by the latter two centers, whereas catalysis by either iron state persists, but in modified form (see below). The abbreviated representation of the overall 5:2 stoichiometry

$$5H_2A + 2Cr^{IV}(dien)(O_2)_2 + 6H^+ \rightarrow 2(dien)Cr^{III} + 5A + 8H_2O \qquad (6)$$

omits an important feature: both ascorbate and acetate from the reaction medium appear in the coordination sphere of the resulting Cr(III) product, with the extent of such incorporation dependent on the concentrations of these anions in the generating solution. Since Fe(II) is very rapidly oxidized ($k = 1.4 \times 10^4\ M^{-1}\ s^{-1}$ at 19°C) by this Cr(IV) oxidant [24], catalysis by Fe(II) and Fe(III) may be taken to utilize a common pathway.

Although the rate laws governing catalysis by Fe(III), Cu(II) and VO^{2+} differ in detail [24,25] (reflecting minor differences in speciation relationships pertaining to the catalytic metal centers), they conform to a common picture. Kinetic saturation with respect to ascorbate (HA^-) is observed in all cases, allowing estimation of association quotients (K_{assn}) for 1:1 cat(HA^-) complexes which are formed: $Fe^{III}(HA^-)$, 5×10^3; $Cu^{II}(HA^-)$, 3×10^2; $VO^{2+}(HA^-)$, 4×10^2 (25°C). However, internal electron transfer within these complexes does not appear to be a significant catalytic step. Such transfers are indeed known for $Fe^{III}(HA^-)$ and $Cu^{II}(HA^-)$ but are found to proceed more slowly than the respective catalyzed $Cr^{IV}(O_2)_2$–ascorbate reactions. Moreover, VO^{2+} does not oxidize ascorbate under catalytic conditions. The kinetic behavior is instead consistent with a bimolecular reaction between the Cr(IV) oxidant and the cat(HA^-) complex, a process which is rate determining for each of the catalyses. These reactions are presumably $1e^-$ transactions yielding the radical $HA^{\cdot}$, subsequent oxidation of which is rapid in each instance. It appears that the three catalytically active cations assume similar roles in these systems, i.e. polarization of ascorbate (via chelation) prior to attack by $Cr^{IV}(dien)(O_2)_2$.

Addition of EDTA to the Fe(III)-catalyzed system greatly alters the mechanistic picture [24]. With ascorbate in excess the decay of Cr(IV) proceeds at constant speed (zero order) during most of the reaction, indicating that the oxidant has become a scavenger, reacting rapidly with an intermediate formed from catalyst and reductant. The observed rate law under these conditions points to the sequence (7)–(10), with the rate determined by generation of the radical $HA^{\cdot}$ (reaction (8)):

$$Fe^{III}(EDTA) + HA^- \rightleftharpoons Fe^{III}(EDTA)(HA^-) \qquad (K = 88\ M^{-1}) \qquad (7)$$

$$Fe^{III}(EDTA)(HA^-) \rightarrow Fe^{II}(EDTA) + HA^{\cdot} \qquad (k = 43\ s^{-1}) \qquad (8)$$

$$HA^{\cdot} + Cr^{IV}(O_2)_2 \rightarrow Cr^{III}(O_2)_2 + A + H^+ \qquad \text{(rapid)} \qquad (9)$$

$$Fe^{II}(EDTA) + Cr^{IV}(O_2)_2 \rightarrow Cr^{III}(O_2)_2 + Fe^{III}(EDTA) \qquad \text{(rapid)} \qquad (10)$$

At low ascorbate concentrations the effective bimolecular rate constant for the Fe^{III}

(EDTA)–HA$^-$ reaction may be calculated as K_6k_7 or 3.8×10^3 M^{-1} s^{-1}, a value near that reported by Taqui Khan and Martell [27] in chromium-free systems under similar conditions.

The preassociation step (7) is almost certainly an inner-sphere event, since the association constant of 88 M^{-1} is too large for an outer-sphere complex between two negatively charged species, and there is evidence that EDTA, although normally sexadentate, occupies, on coordination with transition metal ions, only five positions, leaving the sixth bound to donor water (see e.g. ref. 28) which is easily lost. It appears that EDTA-bound Fe(III) with only one available coordination site, is much less effective than aquo-bound Fe(III) in polarizing ligating ascorbate prior to attack by $Cr^{IV}(O_2)_2$. When that ordinarily preferred path becomes disfavored, electron transfer from ascorbate to Fe(III) assumes the catalytic burden, although less efficiently. The operation of this less advantageous route may be linked to the formal potential of Fe(II/III) in the proper range.

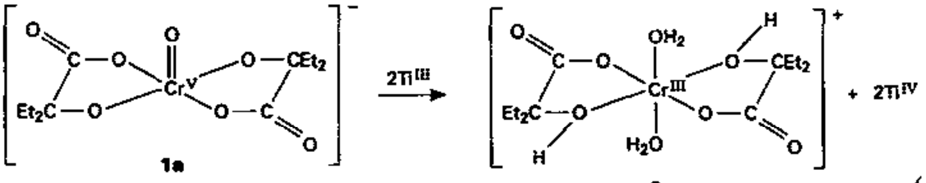
The oxidation of mercapto acids by Cr^{IV}(dien) $(O_2)_2$, as catalyzed by Fe(III), presents a closely related picture [29]:

$$10RSH + 2Cr^{IV}(dien)\,(O_2)_2 + 6H^+ \rightarrow 5R_2S_2 + 2(dien)Cr^{III} + 8H_2O \qquad (11)$$

Here again complexes between the catalyst and the reductant intervene, with K_{assn} for the 1:1 Fe(III)–mercaptoacetate complex greater than 4×10^6 M^{-1}. Once more both buffer anion and mercapto acid anion are incorporated into the Cr(III) product, a feature which has already been attributed to heterolysis of a Cr^{III}(OOH) intermediate.

3. INTERVENTION OF CHROMIUM(IV) IN REDUCTIONS OF CHROMIUM(V)

Reductions of carboxylato-bound chromium(V) with single-electron reductants necessarily pass through a Cr(IV) intermediate. Given favorable circumstances, it is reasonable to anticipate that such an intermediate might be detected and its properties studied. Early experiments using the Cr(V) chelate **1** and Ti(III) [30] confirmed the expected stoichiometry, 2Ti(III)/Cr(V), and the Cr(III) product was found to be unipositively charged with a spectrum corresponding to that of a chelate. The overall reaction may be represented as



1a **6** (12)

The primary Cr(III) species from this reaction is not the thermodynamically favored product, since it undergoes slow aquation even in the presence of excess ligand. Although five stereoisomers (excluding enantiomorphs) may be constructed for dichelates of type **6**, the assigned structure is most clearly related to that of the Cr(V) reactant **1a**.

Kinetic profiles of this Cr^V–Ti^{III} reaction failed to detect evidence for a Cr(IV) transient. The implication here is that any such intermediate reacts much more rapidly with Ti(III) than does the Cr(V) chelate taken as the reactant. Specifically, it may be estimated [30] that the ratio of the two rates must exceed 20 in order that the faster kinetic component go undetected. If structure **6** assigned to the Cr(III) product is correct, the composite electron transfer sequence ($Cr^V \rightarrow Cr^{IV} \rightarrow Cr^{III}$) 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). Analogous conclusions may be drawn from reduction of chelated Cr(V) with Eu^{2+}, during which again no Cr(IV) transient is detected.

Reductions of the Cr(V) chelate **1a** with Fe(II) and VO^{2+} are more informative [31,32]. With these reductants in excess, stoichiometries once more correspond to $2Red^{2+}/Cr(V)$. However, a prominent feature of both reductions is the growth and decay of a Cr(IV) intermediate. In solutions of pH 2–4, with a concentration of the ligating anion (Lig^-) of 0.025 M, this transient makes its appearance as a strongly absorbing species (λ_{max} 511 nm, $\varepsilon = 1.7 \times 10^3$ M^{-1} cm^{-1}). The intervention of this intermediate in both reactions, and in reduction by U(IV) as well [33], the ease with which it is consumed by $1e^-$ reagents in excess and the observation that, like alkoxide complexes of Cr(IV) [11d], it is electron spin resonance (ESR) silent at room temperature support the assigned oxidation state, as does the ESR-monitored titration of Cr(V) with VO^{2+} [32].

The bimolecular specific rate for the Cr^V–Ti^{III} reaction (12) is 5×10^5 M^{-1} s^{-1} (23°C, $\mu = 0.5$ M). This is considerably greater than 10^4 M^{-1} s^{-1}, the estimated [34] substitution-controlled limit for inner-sphere reactions at the Ti(III) center. This difference may be taken as strong evidence that this reaction, and the even more rapid Cr^{IV}–Ti^{III} reaction as well, are predominantly outer sphere. With reductions by Fe(II) and VO^{2+}, specific rates for reductions of Cr(V) and Cr(IV) lie much closer to each other, and with VO^{2+}, Cr(V) reacts somewhat more rapidly than Cr(IV) [32]. A corollary of the Marcus model for outer-sphere reactions [35] is that the ratio of specific rates for 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–VO^{2+} reactions.

The reduction of Cr(V) chelates of type **1** with HSO_3^- [36] was the first of several reactions exhibiting autocatalytic behavior due to intervention of Cr(IV). This system is of additional interest, because with the reductant in excess it displays "clock-like" character, although the net reaction under such conditions involves equimolar quantities of the redox reagents:

$$Cr^{V} + S^{IV} \rightarrow Cr^{III} + S^{VI} \tag{13}$$

Kinetic profiles at two of the wavelengths used to monitor this reaction appear in Fig. 1. In curve B (taken at 385 nm) the principal absorbing species is the Cr(V) chelate **1a**. The rate of consumption of Cr(V) increases slightly during the first 150 s, after which it remains nearly constant until 300 s, finally decreasing during the final stages of reaction. The major portion of curve B points to the operation of an autocatalytic process in which the usual drop in rate due to depletion of a reactant is compensated by the growth of a catalytic species. However, neither of the major products (SO_4^{2-} or the Cr(III) product) exhibits such catalytic action. In addition, a "nick" in curve B occurs 430 s after mixing.

That this "nick" is not an artifact can be shown by monitoring the reaction at 600 nm (curve A). Here Cr(V) and the Cr(III) product have very nearly equal molar absorbances, but the resulting kinetic curve indicates the growth of a strongly

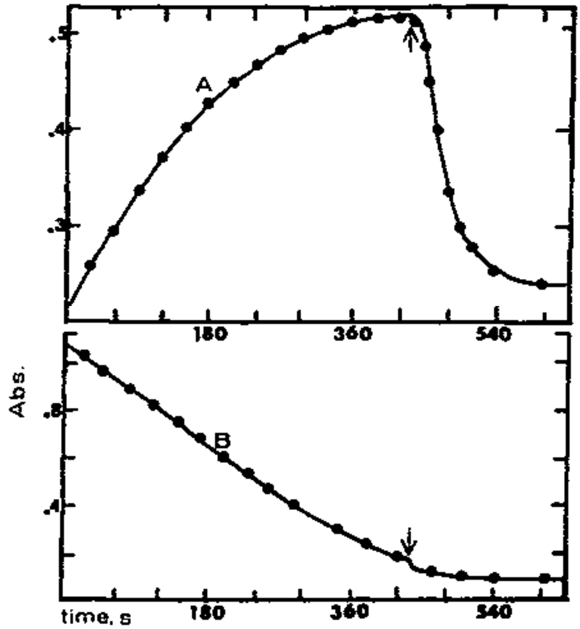


Fig. 1. Kinetic profiles at 600 nm (curve A) and 385 nm (curve B) for reaction of Cr(V) chelate **1** ($R_1 = R_2 = C_2H_5$; 1.10×10^{-3} M) with HSO_3^- (9.7×10^{-3} M) at 21°C. The supporting medium was 0.05 M each in 2-ethyl-2-hydroxybutanoic acid and its sodium salt. Optical path lengths were 5.00 cm for curve A and 1.00 cm for curve B. The solid lines are experimental curves, whereas the small circles represent absorbance changes calculated from sequence (14)–(17), taking k_1 and k_3 as 0.023 and 3.1 M^{-1} s^{-1} respectively and the ratio k_2/k_4 as 30. Extinction coefficients used (M^{-1} cm^{-1}): (600 nm) Cr(III), 43; Cr(IV), 560; Cr(V), 41; (385 nm) Cr(III), 64; Cr(IV), 255; Cr(V), 970. (Reproduced with permission from Inorganic Chemistry, 25, (1986) 3350. Copyright 1986, American Chemical Society.)

absorbing intermediate during the first 426 s (at which point virtually all Cr(V) is consumed) and then a sudden drop in the concentration of this transient. The sharpness and high degree of reproducibility (with respect to time) allow us to classify this as a "clock reaction", i.e. a system in which a sudden marked change occurs after a precise waiting period. The shape of the profile at 600 nm tells us that the intermediate absorbing at this wavelength is being quickly depleted by a reaction that is inhibited by Cr(V) when the latter is present. This inhibition cannot be due to a reaction of Cr(V) with HSO_3^-, since S(IV) is in excess throughout the reaction. It appears instead that Cr(V) is acting as a scavenger for another (non-chromium) intermediate species present in very small concentrations.

The overall picture strongly indicates that the principal catalytic species is a Cr(IV) complex, present throughout the reaction but destroyed near the end of each run via reduction by S(IV). The gradual growth and disappearance of this complex is depicted in curve A; both the autocatalysis and the unusual spectral features disappear when Ce(III) is added to the mixture, reflecting the action of that lanthanide center in catalyzing the disproportionation of Cr(IV) [37].

The reaction series given as (14)–(17), but no simpler sequence that readily comes to mind, is in accord with qualitative and quantitative observations on the Cr^V–HSO_3^- system:

$$Cr^V + S^4 \xrightarrow{k_1} Cr^{IV} + S^5 \qquad (S^4 \equiv HSO_3^-) \tag{14}$$

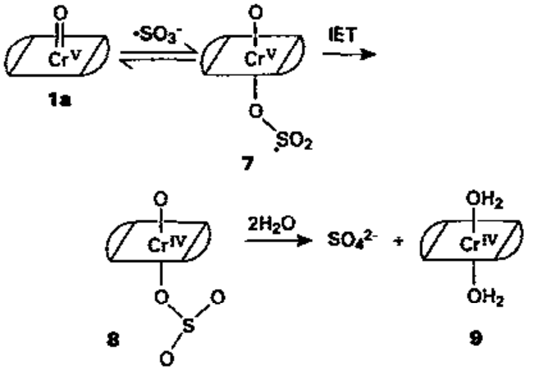
$$Cr^V + S^5 \xrightarrow{k_2} Cr^{IV} + S^6 \qquad (S^6 \equiv SO_4^{2-}) \tag{15}$$

$$Cr^{IV} + S^4 \xrightarrow{k_3} Cr^{III} + S^5 \tag{16}$$

$$Cr^{IV} + S^5 \xrightarrow{k_4} Cr^{III} + S^6 \tag{17}$$

Each step is a single-electron transaction and the sequence involves not only Cr(IV) but also the $SO_3^{\cdot -}$ radical anion (abbreviated S^5) (see e.g. ref. 38). At the beginning of the reaction only (14) and (15) take place, but as Cr(IV) accumulates, (16) assumes importance, yielding an increased concentration of the S^5 radical anion. The shapes of the curves indicate that S^5 reacts more rapidly with Cr(V) than with Cr(IV), but reaction with Cr(V) regenerates Cr(IV) via (15) (hence the autocatalysis). When Cr(V) is exhausted, only (16) and (17) occur, resulting in the nearly pseudo-first-order consumption of Cr(IV). When the steady state approximation is applied to S^5, numerical integration [36,39] of differential equations generated by (14)–(17) 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 as 30, along with extinction coefficients of the three oxidation states of chromium (at 600 and 355 nm) determined independently.

Note that the ratio of reactivities of Cr(V) and Cr(IV) toward HSO_3^- (k_1/k_3) is found to vary from 0.006 to 0.011, being slightly dependent on the acidity and the concentration of the chelating ligand in the medium. This range falls below the estimated upper limit of 0.05 for the analogous ratio pertaining to the outer-sphere reductions of Cr(V) and Cr(IV) by Ti(III) [30] and hence is consistent with an outer-sphere mechanism for both HSO_3^- reactions, although it does not demand this [40]. The corresponding rate ratio for reactions of Cr(V) and Cr(IV) with the radical anion $SO_3^{\cdot -}$ ($k_2/k_4 = 20$–35) points to an inner-sphere path for the Cr^V–S^5 reaction (15). The latter is represented schematically as



in which formation of the precursor complex 7 from the $SO_3^{\cdot -}$ radical anion and the Cr(V) chelate **1a** precedes internal electron transfer (IET) to form a Cr^{IV}–S^{VI} intermediate **8** which features an electron-deficient sulfur atom. Complex **8** then undergoes rapid hydration (at sulfur) and aquation (at Cr(IV)) to yield the $Cr^{IV}(H_2O)_2$ complex **9**. Why such a mechanism (or one related to it) is favored for the Cr^V–S^5 reaction but not for the remaining steps in the proposed series remains an unanswered question. Note, however, that Cr^V–S^5 may be the only one of the proposed steps that involves interaction between a radical and an oxo-bound chromium center, $Cr^V(=O)$.

Autocatalytic behavior analogous to that described for the Cr^V–HSO_3^- system has been observed when the Cr(V) chelate **1a** is reduced by iodide [41], nitrite [42], ascorbate [43], mercapto-substituted carboxylic acids [44], arenediols (hydroquinone and 2,3-dihydroxybenzoic acid [45] and the dinuclear Mo(V) species $Mo_2O_4^{2+}$ [46]. Each of these reductants may be considered as ambifunctional reagents capable of donating either one or two electrons, just as Cr(V) may in principle accept either one or two electrons. In each case sequences related to (14)–(17) may be applied, each involving (A) single-electron oxidations of the reductant to an odd-electron (radical) species by both Cr(V) and Cr(IV) (reactions (14) and (16)) and (B) competition for this radical between Cr(IV) and Cr(V). As with the Cr^V–HSO_3^- system, differential equations based on such sequences reproduce the observed kinetic profiles in each case.

Results for these autocatalytic systems are compared in Table 1. Dramatic autocatalysis and clock-like kinetic traces (related to the consumption of Cr(IV)) generally reflect marked reversals in selectivities toward Cr(V) and Cr(IV) when the primary reductants are compared with the radicals which they generate, i.e. when the differences between the ratios k_1/k_3 and k_2/k_4 (sequences (14)–(17)) are most striking. There is less variation in k_2/k_4 than in k_1/k_3, and in most instances the importance of autocatalysis is determined principally by the selectivity of the primary reductant taken. Reduction by hydroquinone (which proceeds through semiquinone) is exceptional in this respect, since k_1/k_3 lies close to the corresponding ratio for iodide, a strongly autocatalytic reductant. Were it not for the poor selectivity of the semiquinone radical, the hydroquinone system should also exhibit clock-like behavior. Similar autocatalysis in the reduction by hypophosphite ($H_2PO_2^-$), although not dramatic [47], is of particular interest since it implies the intervention of $H_2PO_2^{\cdot}$, a species which is derived in the formal sense from P(II), a rarely encountered oxidation state (see e.g. ref. 48).

Farrell and Lay [9] have recently questioned the assignment of the +4 oxidation state to the chromium intermediates observed when carboxylato chelates of Cr(V) are reduced with Fe(II), VO^{2+}, U(VI) or, in autocatalytic systems, by the reagents listed in Table 1. The latter authors suggest instead that these might be

TABLE 1

Autocatalytic reductions of chelated chromium(V) passing through chromium(IV)[a]

Reductant (Red)	Radical (Red$^\cdot$)	k_1/k_3[b]	k_2/k_4[c]	Ref.
A. Strongly autocatalytic systems exhibiting clock-like behavior				
Bisulfite	$HSO_3^{\cdot -}$	0.005–0.01	20–35	[36]
Ascorbate (HA^-)	$HA^\cdot$	0.005–0.01	7–19	[43]
Iodide	$I^\cdot$	0.017–0.03	40–50	[41]
B. Weakly autocatalytic systems				
Nitrite	NO_2	20–50	3–10	[42]
Thiolactate	$RS^\cdot$	0.1–0.4	2–8	[44]
Cysteine	$RS^\cdot$	0.1–0.5	6–15	[44]
Hydroquinone (H_2Q)	$HQ^\cdot$	0.01–0.04	1–2	[45]
$Mo_2O_4^{2+}$	"$Mo^{V/VI}$"	0.02–0.03	2–4	[46]
Hypophosphite	$H_2PO_2^\cdot$	0.16–0.3	2–3	[47]

[a] Reactions of bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) (chelate **1a**) in aqueous media, pH 2–4. Solutions were buffered with 2-ethyl-2-hydroxybutanoic acid and its anion.

[b] Relative rates at which the primary reductant reacts via 1e$^-$ transfer with the Cr(V) reactant and the Cr(IV) intermediate.

[c] Relative rates at which the radical intermediate reacts via 1e$^-$ transfer with the Cr(V) reactant and the Cr(IV) intermediate.

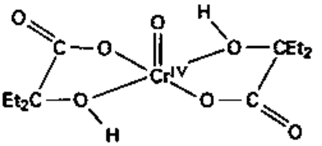
mixed valence (Cr(IV/V)) species formed by reduction of dimeric binuclear $(Cr^{V})_2$ complexes analogous to those derived from perfluoropinacol [49] and pentamethylcyclopentadiene [50]. However, evidence is not yet at hand that dimeric complexes are present in the Cr(V) solutions used in these aqueous redox studies, although small concentrations of such dimers cannot be ruled out. More importantly, the characteristics of such intermediates are found to correspond closely to those of Cr(IV) species formed from action of the $2e^-$ reductant As(III) on Cr(VI) (see following section) in similar media, reactions in which Cr(V) plays no part. In addition, reactions proceeding via a $(Cr^{V})_2$ species in mobile equilibrium with a predominant concentration of Cr(V) monomer would be expected to exhibit a second-order dependency in $[Cr^{V}]$, and this has not yet been reported.

4. STABILIZATION OF CARBOXYLATO-BOUND CHROMIUM(IV)

Although Cr(IV) complexes of 2-hydroxycarboxylates are detected as transients when Cr(V) chelates such as **1** are reduced, either with certain $1e^-$ reagents or with species that can undergo both one- and two-electron oxidations (Table 1), the study of such systems is complicated by the further rapid reductions of Cr(IV) by $1e^-$ transactions.

In 1990–1991 Ghosh and co-workers reported the preparation of more stable Cr(IV) complexes in solution by treatment of $HCrO_4^-$ with a series of $2e^-$ reductants in aqueous media buffered by 2-ethyl-2-hydroxybutanoic acid, $[(C_2H_5)_2C(OH)COOH]$ (HLig), and its anion (Lig^-) [51–54]. Reductions with As(III) yielded the most straightforward results, but reactions with U(IV), HSO_3^- and Sn(II) were also effective. The resulting pink solutions, exhibiting $\varepsilon_{511}^{max} = 2.3 \times 10^3\ M^{-1}\ cm^{-1}$ at high concentrations of the ligating anion (Lig^-), are stable enough to be examined using conventional mixing techniques. There are two keys to this improved stability: (1) the complex must be formed by a $2e^-$ reduction of Cr(VI) rather than by a $1e^-$ reduction of Cr(V) to avoid the rapid $1e^-$ reduction of Cr(IV) following its generation; (2) the carboxylato ligand used to stabilize Cr(IV) must be attached to the Cr(VI) reagent prior to the reduction process.

Since this Cr(IV) complex is oxidized to **1**, a familiar bis(chelate) of Cr(V), in the presence of excess Cr(VI) and is reduced at low $[Lig^-]$ to a bis(chelate) of Cr(III) by a series of $1e^-$ reductants [55], it too may be taken to be a bis(chelate), with structures **10** and **11** coming to mind.



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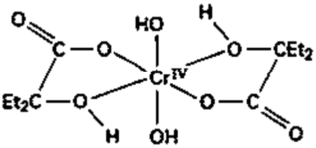

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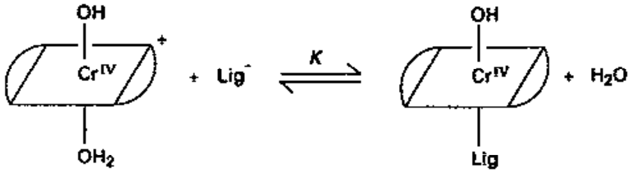
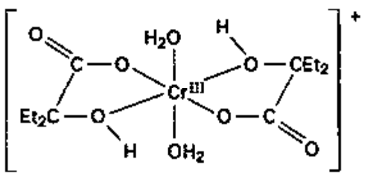
The spectra of Cr(IV) solutions are $[H^+]$-dependent between pH 2 and 5; treatment of absorbance data in this range [32] leads to a pK_A value of 3.4 (23°C, $\mu = 0.4$ M), suggesting protonation of one of the Cr(IV)-bound OH groups in **11**. The absorbance also rises markedly as the concentration of ligand buffer is increased (at constant pH), indicating partition of Cr(IV) between two ligation levels differing by one unit of ligand anion. If the "less ligated" form is the protonated bis(chelate) **12**, this equilibrium may be represented as in which the "extra" ligand coordinates in a unidentate manner. The variation in absorbance with $[Lig^-]$ yields a ligation constant $K_L = 90\ M^{-1}$ at 23°C. This distribution between forms is reflected also in Cr(IV) redox chemistry [55]. Reductions at low $[Lig^-]$ yield as a principal Cr(III) product a +1 cation with the spectrum of a bis(chelate), **14** [32], whereas at higher concentrations of ligand the product is a more strongly absorbing product with properties corresponding to an uncharged "extraligated" complex, **15**.



12 **13**



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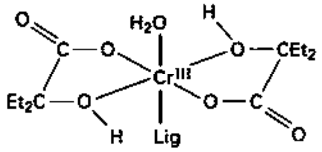

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The pink Cr(IV) solution is formed also from excess Cr(VI) when reductions are carried out, under similar conditions, with Sn(II), HSO_3^-, $Mo_2O_4^{2+}$ or U(IV) [54], each of which is generally considered to be a $2e^-$ reagent. Yields of Cr(IV) are, however, measurably lower than with As(III), and ESR studies of the resulting mixtures immediately after very rapid reaction (Table 2) point to the formation of significant and reproducible amounts of the Cr(V) chelate **1a**, quite apart from that eventually formed in the much slower Cr^{VI}–Cr^{IV} reaction which follows. Analyses of the electronic spectra of these systems lead to the same conclusion: aside from As(III), which may be considered the "purest" of the $2e^-$ reductants chosen, treatment of Cr(VI) with each of the other reagents results in competing $2e^-$ and $1e^-$ transactions, yielding respectively Cr(IV) and Cr(V) complexes.

The reduction with U(IV), which proceeds in part through the unusual state U(V), has been examined in greatest detail [54]. Here a third oxidation state, Cr(III), is rapidly formed in quantity very nearly equal to Cr(V). However, it cannot

TABLE 2

Immediate formation of Cr(V) from reductions of $HCrO_4^-$ using "two-electron reductants". ESR experiments[a]

Reductant	$[Cr^{VI}]$ (mM)	[Red] (mM)	$[Cr^V]$ (mM)[b]	$[Cr^V]/[Red]$
As(III)	1.00	0.50	<0.005	<0.01
U(IV)	2.00	0.50	0.10	0.20
	4.00	0.50	0.096	0.19
	2.00	1.00	0.192	0.19
$Mo_2O_4^{2+}$	1.00	0.50	0.080	0.16
HSO_3^-	1.00	0.50	0.023	0.046
Sn(II)	0.32	0.16	0.069	0.43

[a] Reactions were carried out in solutions 0.05 M each in 2-ethyl-2-hydroxybutanoic acid and its sodium salt (pH 3.3).

[b] Estimated from intensity of the ESR signal at $g = 1.98$, extrapolated to 1 s after mixing.

result from the Cr^{IV}–U^{IV} reaction, which is much slower, nor from the Cr^V–U^{IV} reaction, which has been shown to proceed through Cr(IV) [33]. It must instead be produced from the rapid reaction between U(V) and Cr(IV). The preliminary phase of the overall reaction then entails the three redox components

$$Cr^{VI} + U^{IV} \rightarrow Cr^{IV} + U^{VI} \tag{20}$$

$$Cr^{VI} + U^{IV} \rightarrow Cr^{V} + U^{V} \tag{21}$$

$$Cr^{IV} + U^{V} \rightarrow Cr^{III} + U^{VI} \qquad \text{(rapid)} \tag{22}$$

When Cr(VI) is in excess, the final stage of reaction is the slow comproportionation reaction

$$Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V} \tag{23}$$

a reaction which has been examined in several additional systems.

It has long been recognized that reductants characteristically regarded as $2e^-$ donors can be induced to undergo single-electron changes, given sufficient driving force and the absence of complementary oxidants (see e.g. ref. 56). An even greater degree of flexibility is observed when such reagents are used to reduce Cr(VI) in solutions buffered with those α-hydroxy acids which stabilize both Cr(IV) and Cr(V), since even with a facile two-unit route at hand, U(IV), $Mo_2O_4^{2+}$, HSO_3^- and (most unexpectedly) Sn(II) are seen to utilize minor but perceptible single-electron paths.

In a related study Bose et al. [57] have found that reduction of Cr(VI) by the thiol-substituted tripeptide glutathione, **16**, yields as a major product a Cr(IV) complex (characterized by its magnetic susceptibility), along with a minor amount (less than 5%) of a Cr(V) complex (identified by its ESR signal). In this reaction glutathione (added in excess) serves as a reducing agent, a complexing agent and a

TABLE 3

Mechanistic features of reductions of chelated chromium(IV)[a]

Reductant (R)	Predominant reactive oxidizing species	Predominant reactive reducing species	k (M^{-1} s^{-1}), predominant route(s)[b]	Ref.
A. Estimated from successive 1e⁻ reductions of Cr(V)				
Ti(III) (pH 1)	?	$Ti(OH)^{2+}$	$>1\times10^{7}$ (23°C)	[30]
Fe(II)	$Cr^{IV}(Lig)_2$	Fe^{2+}	3×10^{4} (21°C)	[31]
V(IV)	$Cr^{IV}(Lig)_2(-H^+)$	VO^{2+}	8×10^{2} (21°C)	[32]
Eu(II)	?	Eu^{2+}	$>5\times10^{7}$ (21°C)	[32]
B. Estimated from autocatalytic reductions of Cr(V)				
HSO_3^-	$Cr^{IV}(Lig)_2$	HSO_3^-	1.5–4.1[c]	[36]
$H_2PO_2^-$	$Cr^{IV}(Lig)_2$	$H_2PO_2^-$	0.16 (25°C)	[47]
I^-	$Cr^{IV}(Lig)_2$ & $Cr(Lig)_2H^+$	I^-	0.029, >6 (25°C)	[41]
Ascorbic acid (H_2A)	$Cr^{IV}(Lig)_2$	HA^-	2×10^{5} (24°C)	[43]
NO_2^-	$Cr^{IV}(Lig)_2$ & $Cr(Lig)_2H^+$	NO_2^-	0.05, >8 (25°C)	[42]
Thiolactic acid	$Cr^{IV}(Lig)(H_2O)$	$CH_3CH(SH)COOH$	150 (22°C)	[44]
Cysteine	$Cr^{IV}(Lig)_2$	$HSCH_2CH(NH_3^+)COOH$	2–5[c] (22°C)	[44]
Hydroquinone (HQ)	$Cr^{IV}(Lig)_2$	HQ	2×10^{2} (24°C)	[45]
2,3-Dihydroxybenzoic acid (DHB)	$Cr^{IV}(Lig)_2$	DHB	6.8×10^{-2} (25°C)	[45]
C. Reactions of Cr(IV) solutions generated by the Cr$^{(VI)}$–As$^{(III)}$ reaction				
$IrCl_6^{3-}$	$Cr(Lig)_2$ & $Cr(Lig)_3^-$	$IrCl_6^{3-}$	41 & 90 (25°C)	[55]
$Fe(CN)_6^{4-}$	$Cr(Lig)_2$	$Fe(CN)_6^{4-}$	2×10^{6} (25°C)	[55]
$Fe(4,4\text{-}Me_2bipy)_3^{2+}$	$Cr(Lig)_2$	Fe(II)	1.5×10^{4} (25°C)	[55]
$Fe(5,6\text{-}Me_2phen)_3^{2+}$	$Cr(Lig)_2$	Fe(II)	9×10^{2} (25°C)	[55]
$H_2AsO_3^-$			No reaction	[52]
U(IV)	$Cr(Lig)_2$	$U(lig)^{3+}$	2×10^{3} (24°C)	[54]
Sn(II)	$Cr(Lig)_2$ & $Cr(Lig)_2(-H^+)$	Sn^{2+}	3×10^{2} & 1×10^{2} (25°C)	[58]
$(Mo^V)_2$	$Cr(Lig)_2$	$(Mo^V)_2$ activated	d	[52]

D. Additional reactions				
$2Cr^{IV} \rightarrow Cr^{III} + Cr^{V}$				
(uncat.)	$Cr(Lig)_2(-H^+)$	$Cr(Lig)_2(-H^+)$	1.8×10^2 (25°C)	[64]
(Mn^{2+} cat.)	$Cr(Lig)_2$	Mn^{2+})	0.38 (25°C)	[64]
(Ce^{3+} cat.)	$Cr(Lig)_2$	Ce^{3+}	4.0^{e} (25°C)	[58]
$Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V}$	$Cr(Lig)_2$	$HCrO_4^-$	2.2 (25°C)	[52,54]

---

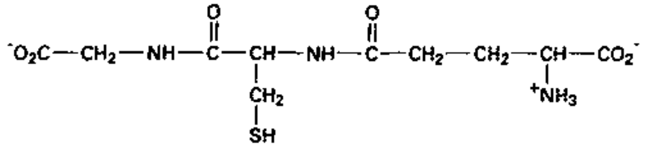
[a] Reactions of Cr(IV) chelate **11**; pH 2–4; μ was generally 0.5 M. "Lig^-" = 2-ethyl-2-hydroxybutyrate.

[b] Second-order rate constants. Where chemical saturation is observed, given values apply to low reagent concentrations where reactions approximate second order.

[c] k varies with $[H^+]$ and/or $[Lig^-]$, but data are not precise enough to establish complete rate law.

[d] Rate is $5 \times 10^2[R]$, independent of $[Cr^{IV}]$.

[e] Disproportionation reaction is accompanied by Ce(III)-catalyzed oxidation of HLig to $CO_2 + Et_2C{=}O$.



$$^{-}O_2C{-}CH_2{-}NH{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{\underset{SH}{|}}{CH_2}}{\underset{|}{CH}}{-}NH{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}\underset{\underset{^{+}NH_3}{|}}{CH}{-}CO_2^{-}$$

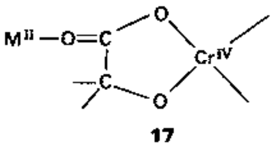
16

buffer. Slow reductions of the Cr(IV) and Cr(V) intermediates then yield Cr(III) species ligated by both glutathione and its disulfide oxidation product.

5. REDOX REACTIONS OF CHROMIUM(IV) COMPLEXES

Table 3 summarizes the features of a number of reductions of bis(chelated) Cr(IV) thus far examined. Where more than one mechanistic path operates, only species participating in the principal route are generally listed. To facilitate comparison, bimolecular rate constants for these routes are tabulated. In those cases where kinetic saturation is observed, *k* values pertain to low reagent concentrations where reactions approximate second-order behavior. Among these entries we see a wide range in reaction rates and considerable variation with respect to selectivity among ligation and protonation levels of the Cr(IV) oxidant. Presumably both inner- and outer-sphere mechanisms operate, but a choice between these is not always possible.

Inner-sphere routes may well be favored for the rapid reductions by substitution-labile metal centers (Section 1), since each of these may form a bridged activated complex of type **17**, except, as noted, Ti(III), for which substitution at the reducing center is slower than the redox reaction. Since the transition states for the predominant routes are not analogous, these systems are not strictly comparable. Nevertheless, it appears that the trend in rates is set principally by the formal potentials of the reductants.



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Of the non-metallic "ambifunctional" reagents in Section 2, each undergoes the loss of one electron in reaction with Cr(IV). Rate constants listed here are derived from multivariant analyses of autocatalytic curves and must be considered much less precise than those pertaining to simpler systems involving just one or two adjustable parameters. For reductions with HSO_3^- and cysteine, variations in *k* with $[H^+]$ or $[Lig^-]$ were noted, but data at hand were not sufficient to define detailed rate laws.

As a group, these reductions are substantially slower than those by metal ions and may proceed through "ester-like" intermediates formed by coordination of the reductant at a substitution-labile Cr(IV) center, in much the same way that substitution at Cr(VI) precedes its reduction to bis(chelated) Cr(IV) and Cr(V). The detailed kinetic picture associated with the most rapid reductant in the group, ascorbate [43], points to the intervention of such a complex $Cr^{IV}(HA^-)$ ($K_{assn} = 110\ M^{-1}$), within which internal electron transfer ($k = 2 \times 10^2\ s^{-1}$) proceeds, forming a Cr(III) complex of $HA^{\cdot}$.

Reductions by both I^- and NO_2^- are seen to utilize "extraprotonated" paths, neither of which exhibits kinetic saturation at pH values above 2. Although individual rate constants cannot be evaluated for such routes, lower limits of 6 and 8 $M^{-1}\ s^{-1}$ may be estimated by assuming pK values less than 1.0 for the additional protonation.

The first four reductants in Section 3 are coordinatively saturated and substitution inert. Their oxidations must therefore be outer sphere. The recorded rate constants for these reagents may be used to estimate a self-exchange rate for the Cr(III/IV) couple (Section 7).

The Cr^{IV}–U^{IV} reaction is of particular interest because it proceeds through the unusual state U(V), which, as we have noted, reacts rapidly with an unconsumed unit of Cr(IV) (reaction (22)). The activated complex for the principal route has a composition $U^{IV}(Lig)Cr^{IV}(Lig)_2$ and the overall reaction is retarded by excess ligand anion and increasing acidity. Of several sequences consistent with the observed kinetic pattern [54], the most reasonable appears to be (24)–(29) followed by (22):

$$U^{IV} + Lig \rightleftharpoons U^{IV}(Lig) \qquad (K > 10^4) \tag{24}$$

$$U^{IV}(Lig) + H^+ \rightleftharpoons U^{IV}(LigH) \qquad (pK_A = 2.06) \qquad \text{(inactive)} \tag{25}$$

$$U^{IV}(Lig) + Lig \rightleftharpoons U^{IV}(Lig)_2 \qquad (K_{assn} = 60) \qquad \text{(inactive)} \tag{26}$$

$$U^{IV}(LigH) + Lig \rightleftharpoons U(LigH)(Lig) \qquad (K_{assn} = 370) \qquad \text{(inactive)} \tag{27}$$

$$U^{IV}(Lig) + Cr^{IV}(Lig)_2 \rightleftharpoons U^{IV}(Lig)Cr^{IV}(Lig)_2 \qquad (K_p = 5 \times 10^3) \tag{28}$$

$$U^{IV}(Lig)\ Cr^{IV}(Lig)_2 \rightarrow U^V + Cr^{III}(Lig)_3 \qquad (k = 0.20\ s^{-1}) \tag{29}$$

$$U^V + Cr^{IV} \rightarrow U^{VI} + Cr^{III} \qquad \text{(rapid)} \tag{22}$$

Here the pool of the suggested "precursor" (formed in (28)) is partially depleted by protonation (eqn. (25)) and "extraligation" (eqns. (26) and (27)). The limiting bimolecular rate constant for this reaction (Table 3) is twice the product $K_p k$, reflecting the rapid "follow-up reaction" (22).

The reduction of chelated Cr(IV) by Sn(II) [58]

$$2Cr^{IV} + Sn^{II} \rightarrow Sn^{IV} + 2Cr^{III} \tag{30}$$

results in a net change suggesting a "non-complementary reaction" involving a $1e^-$ reduction of Cr(IV) in conjunction with a $2e^-$ oxidation of Sn(II). Such reactions are proverbially very slow unless a path exists in which each step allows redox partners to undergo matching transactions. Two mechanisms for this transformation come to mind, each featuring an initial slow step and a rapid follow-up step. The first,

$$\mathrm{Sn^{II}+Cr^{IV}\rightarrow Sn^{IV}+Cr^{II}} \tag{31}$$

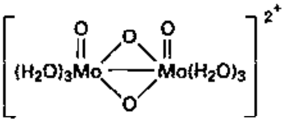
$$\mathrm{Cr^{II}+Cr^{IV}\rightarrow 2Cr^{III}} \quad \text{(rapid)} \tag{32}$$

entails the intervention of the familiar state Cr(II), whereas the second,

$$\mathrm{Sn^{II}+Cr^{IV}\rightarrow Sn^{III}+Cr^{III}} \tag{33}$$

$$\mathrm{Sn^{III}+Cr^{IV}\rightarrow Sn^{IV}+Cr^{III}} \quad \text{(rapid)} \tag{34}$$

passes through the very unusual state Sn(III) (see e.g. ref. 59). The potential for the $\mathrm{Cr^{IV}\rightarrow Cr^{II}}$ conversion (31) is favorable. Moreover, the next reaction is markedly inhibited by a series of oxidants of the type $\mathrm{(NH_3)_5Co^{III}X}$ ($X \equiv$ Cl, Br, N_3, pyrazine) which are known to react very rapidly ($k > 10^5\ \mathrm{M^{-1}\,s^{-1}}$) with Cr(II) [60]. The relative effectiveness of these Co(III) inhibitors corresponds closely to the measured rates at which they oxidize $\mathrm{Cr^{2+}}$, pointing strongly toward intermediacy of a Cr(II) species (sequence (31)–(32), and in accord with this sequence the rates of reduction of Cr(IV) in the presence of the most effective Co(III) inhibitors approach a value one-half the uninhibited rate. Inhibition by the pyrazine complex is particularly informative, since this heterocyclic ligand is thought to be an effective redox bridge only for d-block centers [60b]. In addition, intervention of Cr(II) has been found to be a distinguishing feature of a number of reductions of aqua-substituted Cr(IV) (see following section).



10 '(Mo^{V})$_2$'

The dimeric molybdenum(V) cation $[\mathrm{Mo_2O_4(H_2O)_6}]^{2+}$ (**10**) is oxidized to 2Mo(VI) with Cr(IV) [51,52]:

$$\mathrm{2Cr^{IV}+(Mo^{V})_2\rightarrow 2Cr^{III}+2Mo^{VI}} \tag{35}$$

This reaction, like (30), is non-complementary but almost certainly proceeds in quite a different fashion, probably via a "mixed valence" intermediate (designated $\mathrm{Mo^{V}Mo^{VI}}$). The most notable facet is a rate proportional to $[\mathrm{(Mo^{V})_2}]$ but independent of $[\mathrm{Cr^{IV}}]$ during a major portion of the transformation, i.e. a rate of consumption of Cr(IV) governed by a reaction not involving a chromium species. The essential step here is probably the unimolecular conversion of $\mathrm{(Mo^{V})_2}$ to an activated form, designated $\mathrm{(Mo^{V})_2^{*}}$, a step that appears to intrude also in the redox reactions of

$(\mathrm{Mo^V})_2$ with the μ-superoxo complex $[(\mathrm{NH_3})_5\mathrm{Co(O_2)Co(NH_3)_5}]^{5+}$ [61] and with $\mathrm{IrCl_6^{2-}}$ and $\mathrm{Fe(phen)_3^{3+}}$ [62], each of which exhibits a prominent oxidant-independent kinetic term. Cayley et al. [62] have suggested that the activation process in such cases is the hydrolytic cleavage of one of the oxo bridges to give an Mo(OH)–Mo(OH) intermediate, and a closely related species has been proposed as an intermediate in the photolytic decomposition of $(\mathrm{Mo^V})_2$ in aqueous solution [63]. The overall conversion may then be represented schematically as

$$(\mathrm{Mo^V})_2 \rightarrow (\mathrm{Mo^V})_2^{*} \qquad \text{(slow)} \tag{36}$$

$$(\mathrm{Mo^V})_2^{*} + \mathrm{Cr^{IV}} \rightarrow \mathrm{Mo^VMo^{VI}} + \mathrm{Cr^{III}} \qquad \text{(rapid)} \tag{37}$$

$$\mathrm{Mo^VMo^{VI}} + \mathrm{Cr^{IV}} \rightarrow 2\mathrm{Mo^{VI}} + \mathrm{Cr^{III}} \qquad \text{(rapid)} \tag{38}$$

Although the anions of α-hydroxy acids have been found to be the most effective ligands for stabilization of Cr(IV) via chelation, the resulting solutions do not persist indefinitely, since they undergo both disproportionation (eqn. (39)) and reduction by the parent ligand (eqn. (40)), with the relative importance of these two modes of attrition dependent on both the acidity of the medium and the nature of added transition metal ions:

$$2\mathrm{Cr^{IV}} \rightarrow \mathrm{Cr^{III}} + \mathrm{Cr^V} \tag{39}$$

$$2\mathrm{Cr^{IV}} + \mathrm{R_2C(OH)\,COO^-} \rightarrow 2\mathrm{Cr^{III}} + \mathrm{R_2C{=}O} + \mathrm{CO_2} + \mathrm{H^+} \tag{40}$$

For Cr(IV) stabilized by buffers of 2-ethyl-2-hydroxybutanoic acid and its anion in the absence of added metal catalysts, only the disproportionation is of importance. Kinetic studies of such systems [64] point to two bimolecular components for this reaction: a major contributor involving two units of the principal deprotonated form of chromium, $\mathrm{Cr^{IV}Lig_2OH}$, and a minor contributor requiring two units of the "extraligated" species $\mathrm{Cr^{IV}Lig_3}$. The predominant route for the uncatalyzed disproportionation may be reasonably represented as the sequence

$$2\mathrm{Cr^{IV}{-}OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{Cr^{IV}{-}O{-}Cr^{IV}} \xrightarrow{\mathrm{IET}} \mathrm{Cr^{III}{-}O{-}Cr^{V}} \xrightarrow{\mathrm{H^+}}$$

$$\mathrm{Cr^{III}{-}OH{-}Cr^{V}} \xrightarrow{\text{rapid}} \mathrm{Cr^{III}OH} + \mathrm{Cr^V} \tag{41}$$

with the step entailing internal electron transfer (IET) being rate determining. For the rapid follow-up step, i.e. dissociation of the Cr(III/V) "successor complex", breakage of the $\mathrm{Cr^V{-}O}$ bond is favored in accord with the greater substitution lability at the $\mathrm{d^1}$ center (see e.g. ref. 65).

Of the usual d- and f-block metal centers, only Mn(II) and Ce(III/IV) catalyze this disproportionation significantly. Catalysis by Mn(II) presents the simpler picture, with the principal route appearing to utilize an activated complex of the type $\mathrm{Cr^{IV}(OH)Mn^{II}}$ ($K_{\mathrm{assn}} = 52$) [64]. This reaction almost certainly passes through

Mn(III) via the sequence

$$Cr^{IV}(OH)\xrightarrow{Mn^{II}}Cr^{IV}\text{–}OH\text{–}Mn^{II}\rightarrow Cr^{III}\text{–}OH+Mn^{III} \tag{42}$$

$$Cr^{IV}(OH)\xrightarrow{Mn^{III}}Cr^{IV}\text{–}OH\text{–}Mn^{III}\rightarrow Cr^{V}\text{–}OH+Mn^{II} \tag{43}$$

The catalytic effectiveness of Mn(II) may then be attributed in part to a formal potential lying within or near the gap between that for Cr(IV/III) in this medium (0.98 V) and that for Cr(V/IV) (about 0.88 V) [66]. If steps (42) and (43) proceed through OH-bridged intermediates, it is further advantageous that ligand substitutions about both Mn(II) and Mn(III) centers proceed more rapidly than those about Cr(IV) (see e.g. ref. 67). In contrast, the couples Ti(IV/III) and Fe(III/II) are without catalytic action, because the higher state in each case is too weakly oxidizing to convert Cr(IV) to Cr(V). Catalysis by second- and third-row transition metal centers is strongly disfavored by their substitution-inert character.

Catalysis by Ce(III) of the disproportionation of chelated Cr(IV) [58] is complicated by Ce(III)-catalyzed oxidation of the ligand (eqn. (40)). The active species in both catalytic processes is presumably Ce(IV), and kinetic studies of this system, in addition to examination of the distribution of reaction products from (39) and (40) at various reagent concentrations, support the sequence (44)–(46) for the catalyzed loss of Cr(IV):

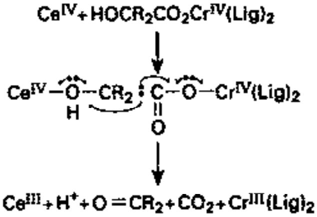
$$Cr^{IV}+Ce^{III}\rightarrow Cr^{III}+Ce^{IV} \tag{44}$$

$$Ce^{IV}+Cr^{IV}(Lig)\rightarrow Ce^{III}+Et_2C{=}O+CO_2+Cr^{III}+H^+ \tag{45}$$

$$Ce^{IV}+Cr^{IV}\rightarrow Ce^{III}+Cr^{V} \tag{46}$$

In this formulation the slow step is taken to be the generation of Ce(IV), which is then partitioned between the two indicated reaction paths. Although rates for the two rapid follow-up reactions could not be measured, the selectivity between paths, i.e. the ratio k_{45}/k_{46}, was found to be very nearly 3/4 at 25°C.

The proposed sequence stipulates that Cr(IV) as well as Ce(IV) is required for oxidation of the ligand (reaction (45). An alternate formulation in which Cr(IV) is omitted from this step does not reproduce the observed pattern of Cr(V) yields. Note that the yields of 3-pentanone ($Et_2C{=}O$) are nearly independent of Lig^- when the latter is in large excess, since oxidation of the ligand involves the complex Cr^{IV} (Lig), the concentration of which under such conditions is determined mainly by Cr(IV) taken rather than by unattached Lig^-. It is reasonable that the Ce^{IV}–Cr^{IV} step (46), like the corresponding Mn^{III}–Cr^{IV} step (43) in the Mn-catalyzed disproportionation, proceeds through an OH-bridged activated complex of the type Ce^{IV}–OH–Cr^{IV}. It is likely, however, that the ligand oxidation by Cr^{IV}–Ce^{IV}, like that of a known series of Co^{III}–Ce^{IV} co-oxidations of closely related ligands [68], is an induced electron transfer process requiring a different configuration and that it is initiated by attachment of Ce(IV) to the hydroxy group of a Cr(IV)-bound ligand. The transformation then is consummated by C–C fragmentation and the two acts of electron transfer to the quadripositive metal centers, with the three concluding events being synchronous or very nearly so: Catalytic complexity in the Cr^{IV}–Ce^{II} system may then be attributed, at least in part, to the long-recognized (see e.g. ref. 69) strong affinity between Ce(IV) and the alcoholic hydroxyl function.



(47)

The slow oxidation of ligated Cr(IV) by Cr(VI) ($Cr^{IV}+Cr^{VI}\rightarrow 2Cr^{V}$) generally intrudes as a "follow-up step" when Cr(IV) is generated by $2e^-$ reduction of excess $HCrO_4^-$ [52]. Such systems feature a Cr^{IV}–Cr^{VI} complex ($K_{assn}=40$) and reaction via a combination of acid-independent and $[H^+]$-proportional paths. When this reaction is carried out in the usual hydroxy acid buffers, it is likely that a ligated form of Cr(VI) is involved, since virtually all of the Cr(V) product, half of which arises from the oxidant, is the familiar bis(chelate) **1**.

Despite the mechanistic diversity associated with reactions of Cr(IV), these conversions appear to have one kinetic characteristic in common, i.e. a negligibly small kinetic salt effect. Thus reactions with $HCrO_4^-$, $IrCl_6^{3-}$ and Sn(II) (coreagents of widely different charge types) are neither accelerated nor retarded when the ionic strength of the reaction medium is increased from 0.10 to 2.0 M [55]. The implication here is that the reacting Cr(IV) species has no net charge, an inference consistent with both suggested structures **10** and **11**.

6. AQUA-SUBSTITUTED CHROMIUM(IV)

Although the importance of Cr(IV) as an intermediate in reductions of Cr(VI) has long been appreciated, aqua-substituted Cr(IV), which may reasonably be taken as a "point of reference" in considering this state, was not detected until 1991 [13]. Each of three methods for its generation involved oxidation of aqueous Cr^{2+}, the first by thallium(III), the second by Adams et al.'s (μ-peroxo)$(Cr^{III})_2$ complex $[CrO_2Cr]^{4+}$ [22] and the third by the superoxochromium(III) complex CrO_2^{2+} (aq) (a novel species in its own right prepared by action of O_2 on very low concentrations of Cr^{2+} [70]). This Cr(IV) cation, formed at maximum concentrations near 10^{-4} M, exhibits an absorption maximum at 260 nm ($\varepsilon=5\times10^3$ M^{-1} cm^{-1}) and decays with a half-life near 30 s in 1 M $HClO_4$ (25°C). At the low concentrations of this ion thus far prepared, maxima in the visible range cannot be detected.

Aquachromium(IV) is represented as an oxo-substituted species $[Cr{=}O]^{2+}$, principally because of a series of $2e^-$ reductions it undergoes, yielding Cr^{2+}. It rapidly oxidizes triphenylphosphine, recognized as a strong oxygen atom acceptor, to the corresponding phosphine oxide:

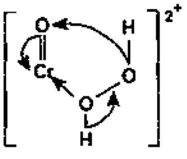
$$CrO^{2+} + (C_6H_5)_3P \rightarrow Cr^{2+} + (C_6H_5)_3P{=}O \tag{48}$$

In addition, oxidations of an array of primary and secondary alcohols and of formic and oxalic acids also yield Cr^{2+} (conveniently detected by monitoring the growth of superoxochromium(III), CrO_2^{2+}, which is formed very rapidly by the reaction of Cr^{2+} with O_2 [71]). Kinetic isotope effects, k_H/k_D, resulting from substitution of D for H at the α positions(s) of such alcohols (e.g. CD_3OH vs. CH_3OH) fall between 2 and 4, indicating that the rate-determining step in such oxidations involves breakage of a C–H bond and removal of hydrogen, either as a hydrogen atom (leaving a radical) or as hydride. However, these oxidations are not substantially accelerated by incorporation at the 2 position of substituents which are known to stabilize carbon radicals (e.g. allyl or a single phenyl). The implication then is that aquachromium(IV) is reacting by extraction of an α-hydrogen with its electron pair (i.e. as hydride), converting the oxidant to a Cr(II) species. Related mechanisms may be applicable to reactions with aldehydes and oxidizable carboxylic acids.

These experiments with aquachromium(IV) bear importantly upon the classical [2] question as to the mechanism of oxidation of secondary alcohols by Cr(VI) ($HCrO_4^-$). Scott et al. [71] find that when this reaction is carried out at low concentrations (10^{-4}–10^{-5} M) of Cr(VI) in the presence of 10^{-3} M dissolved O_2, the superoxo complex CrO_2^{2+} is formed in quantity approaching that of the Cr(VI) taken. Since CrO_2^{2+} presumably arises only from Cr^{2+}, the latter must have intruded in the net reduction of Cr(VI). It is then proposed that Cr(VI) is reduced in a pair of $2e^-$ changes, each producing a molecule of ketone, with the first yielding aquachromium(IV) and the second giving Cr(II). Both acts may then be taken as hydride transfers. Such a sequence stands in contrast with that favored by a number of earlier workers (see e.g. ref. 32) in which Cr(IV), formed in an initial $2e^-$ transaction, was thought then to extract $H^{\cdot}$ from a second molecule of alcohol, yielding a radical $R_2^{\cdot}COH$ and Cr(III). The older suggested mechanism, which makes no provision for the intermediacy of Cr(II), may, however, operate with alcohols such as benzhydrol, $(C_6H_5)_2CHOH$, which, upon homolysis of the α-CH bond, may give a radical greatly stabilized through conjugative interaction with the two phenyl groups.

The reaction of aquachromium(IV) with H_2O_2 [73] also appears to proceed by hydride abstraction. The product is again the superoxo complex CrO_2^{2+}, but this is formed even when O_2 is rigorously excluded from the reaction mixture. The kinetic isotope effect, $k_{H_2O_2}/k_{D_2O_2} = 3.6$, lies very close to that observed in the oxidations of

CH_3OH and CD_3OH [71]. In this case the oxygen in CrO_2^{2+} arises from the H_2O_2. The characteristics of this reaction point to a cyclic transition state **16** in which the hydride transfer to the oxo group of CrO^{2+} and attachment of the O—O fragment to the electron-rich chromium atom are concerted or very nearly so.



16

Aquachromium(IV) is also formed from the reaction of Fe(II) with the hydroperoxochromium(III) complex $(H_2O)_5Cr(O_2H)^{2+}$, the latter resulting from $1e^-$ reduction of the superoxo derivative CrO_2^{2+} using $Ru(NH_3)_6^{2+}$ [74]. In this system CrO^{2+} was detected by trapping with $HC_2O_4^-$ (eqn. (49)). It is also possible to study the (much faster) Fe(II) reduction of CrO^{2+} (eqn. (50)) by generating the latter via the Cr^{II}–Tl^{III} reaction [13].

$$CrO_2^{2+} + HC_2O_4^- \xrightarrow{H^+} Cr^{2+} + 2CO_2 + H_2O \qquad (k = 2 \times 10^3\ M^{-1}\ S^{-1}) \tag{49}$$

$$CrO^{2+} + Fe^{2+} \xrightarrow{2H^+} Cr^{3+} Fe^{3+} + H_2O \qquad (k = 4 \times 10^3\ M^{-1}\ S^{-1},\ 25°C) \tag{50}$$

7. POTENTIALS AND ELECTRON SELF-EXCHANGE RATES INVOLVING CHROMIUM(IV)

To compare further the redox chemistry of chelate-stabilized tetrapositive chromium $[Cr^{IV}(Lig)_2]$ with that of chelated Cr(V) and with related species derived from other metal centers, estimates of both the formal potential and the electron self-exchange rate pertaining to the couple $Cr(Lig)_2^{IV/III}$ are desirable.

In solutions buffered by 2-ethyl-2-hydroxybutanoic acid and its anion, $Cr^{IV}(Lig)_2$ is an oxidant comparable in potential with several tris-chelates of iron derived from methyl-substituted 1,10-phenanthrolines ($Fe(phen)_3^{3+/2+}$ complexes) and 2,2′-bipyridyls ($Fe(bipy)_3^{2+/3+}$ complexes), the formal potentials of which are known [75]. Equilibrium quotients (*Q* values) for reactions of the type

$$Cr^{IV} + [Fe^{II}L_3]^{2+} \rightarrow Cr^{III} + [Fe^{III}L_3]^{3+} \qquad (L \equiv 5,6\text{-}Me_2phen,\ 4,4'\text{-}Me_2bipy) \tag{51}$$

may be evaluated in HLig–Lig⁻ buffers. Since two protons are consumed in the full reactions

$$2H^+ + Cr^{IV}(Lig)_2(OH)_2 + Fe^{II} \rightarrow Cr^{III}(Lig)_2(H_2O)_2^+ + Fe^{III} \tag{52}$$

these quotients should be proportional to $[H^+]^2$. Plots of observed *Q* values *vs.*

$[H^+]^2$ [55] give as slopes the acid-independent K values: $10^{5.5}$ for reduction by $[Fe^{II}(5,6\text{-}Me_2phen)_3]^{2+}$ and $10^{7.3}$ for reduction by $[Fe^{II}(Me_2bipy)_3]^{2+}$. These K values, in combination with the recorded $E°$ values [75] for the reductants, lead to formal potentials of 1.33 and 1.37 V for chelate-stabilized Cr(IV/III).

A similar treatment is possible for chelate-stabilized Cr(V), which is reduced to Cr(III) by the same type of reductants with no evidence for appreciable accumulation of Cr(IV):

$$Cr^V + 2[Fe^{II}L_3]^{2+} \rightarrow Cr^{III} + 2[Fe^{III}L_3]^{3+} \tag{53}$$

The reaction quotient for the Cr^V–$Fe^{II}(Me_2bipy)_3$ reaction, $10^{-0.51}$ at pH 3.3, when adjusted for the attendant consumption of four protons, yields $K_{eq} = 10^{12.9}$, allowing an estimate of $E°$ for Cr(V/III) of 1.32 V. The latter potential, in conjunction with $E°(Cr^{IV/III}) = 1.35$ V, leads to 1.29 V for $E°(Cr^{V/IV})$. Thus Cr(IV) is, as expected, a somewhat stronger $1e^-$ oxidant than Cr(V). This difference is in accord with the observed spontaneous disproportionation of $Cr^{IV}(Lig)_2$ (eqn. (39)), a reaction for which the calculated formal potentials yield an equilibrium quotient of 10 (25°C, pH 3.3). The reduction of Cr(V) by these $1e^-$ reductants must proceed through Cr(IV), but since growth of the latter is not observed in these cases, the initial conversion to Cr(IV) is assumed to be rate determining and the follow-up reduction ($Cr^{IV} \rightarrow Cr^{III}$) is taken to be rapid.

Rate constants for the (necessarily outer-sphere) reductions of Cr(IV) by the first four reagents in Table 3C are 10^3–10^4 times those for the corresponding reductions of Cr(V), a difference which is much too great to reflect merely the gap (0.06 V) between the formal $1e^-$ potentials of the oxidants. The major part of this divergence may then be attributed, using the model of Marcus [35], to a difference in electron self-exchange rates for the couples $Cr^{(IV/III)}$ and $Cr^{(V/IV)}$.

A detailed quantitative treatment [76] of this model represents the rate constant k_{12}, of an outer-sphere electron transfer reaction as the sum of three terms:

$$\ln k_{12} = \frac{1}{2}\left(\ln(k_{11}k_{22}K_{12}) + \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4[\ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT]}\right) + \frac{w_{11} + w_{22} - w_{12} - w_{21}}{2RT} \tag{54}$$

where k_{11} and k_{22} are the self-exchange rates for the oxidant and reductant respectively, K_{12} is the equilibrium constant for the redox reaction, Z is the collision frequency, $10^{11}\ M^{-1}\,s^{-1}$, and the ws are electrostatic work contributions from the reactants, the products and the two self-exchanging systems. Each w term is calculated in turn by

$$w_{cd} = 4.23\,\frac{z_c z_d}{a_{cd}}\,(1 + 0.33 a_{cd}\mu^{1/2}) \tag{55}$$

where the zs are the ionic charges on interacting species c and d, μ is the ionic strength of the medium and a_{cd} is the distance of closest approach, as estimated from the presumed geometry of the encounter and the reported atomic and ionic radii.

Values of k_{12} for the "cross-reactions" involving Cr(IV) and those for Cr(V) are listed in Table 4, along with parameters contributing to eqn. (4). In those few cases where kinetic components from both the oxidant and its extraligated form (e.g. $Cr^{IV}(Lig^-)$) have been detected, the rate constant associated with the former has been chosen.

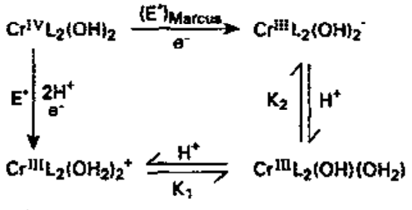
At 25°C $\log K_{12}$ may be taken as $\Delta E°/0.059$. However, the Marcus model requires that the partners in each of the contributing half-reactions differ only in their electron count and not in their level of protonation. Since the predominant Cr(III) product from the Cr(IV) reactions, $Cr^{III}(Lig)_2(H_2O)_2{}^+$, has two more protons than the Cr(IV) oxidant (eqn. (52)), the estimated $E°$ for Cr(IV/III), 1.35 V, must be converted to a value pertaining instead to $Cr^{III}(Lig)_2(OH)_2{}^-$. The treatment, analogous to that by Macartney [77], utilizes the steps indicated in Scheme 1 and leads to (56), where the Ks represent successive acidity constants for the reduced form:

$$(E°)_{Marcus} = E° - 0.059\ (pK_1 + pK_2) \tag{56}$$

Combining the experimental value of pK_1 (3.4) and an estimate of pK_2 [55] leads to an estimated "electron-exchange-only" potential $(E°)_{Marcus}$, of 0.81 V for Cr(IV/III). The corresponding treatment of the $E°$ value for Cr(V/IV), 1.29 V, in conjunction with the reported [32] pK_1 of 3.5 for Cr(IV), yields a potential $(E°)_{Marcus} = 0.72$ V pertaining to single-electron transfer from the Cr(V) oxidant **1** ($R_1 \equiv R_2 \equiv C_2H_5$).

Values of k_{12} for Cr(IV), in combination with (54), lead to a calculated electron self-exchange rate k_{11} of $10^{-0.51 \pm 0.40}$ $M^{-1}\ s^{-1}$ for Cr(IV/III). The indicated uncertainty is comparable with those estimated earlier for other systems featuring transition metal centers [77,78].

The Cr(IV/III) rate falls within the span characteristic of several octahedral aqua complexes of 3d block centers ($[TiOH]^{3+/2+} \geqslant 10^{-3.5}$ $M^{-1}\ s^{-1}$; $V^{3+/2+}$, $10^{-2.0}$; $Mn^{3+/2+}$, $10^{-3.5}$; $Fe^{3+/2+}$, $10^{0.1}$), but lies substantially above that for $Cr^{3+/2+}$ ($\leqslant 10^{-4.7}$) [76,79]. The low value for the latter is generally attributed to Jahn–Teller elongation of axial metal–ligand bonds in the reduced (d^4) member of this system [79]. The overall similarity suggests that aside from $Cr^{3+/2+}$, the Franck–Condon



Scheme 1.

TABLE 4

Calculated self-exchange rates and contributing parameters for redox reactions involving Cr(IV), Cr(V) (bis(chelate) 1: $R_1{\equiv}R_2{\equiv}C_2H_5$), V(IV) and V(III) (25°C)

Oxidant	Reductant	μ (M)	E°_{red}	LogK_{22}[a]	LogK_{12}[b]	LogW_{12}[c]	k_{12}	Logk_{11}[d]
Cr(IV)[e] (E° 0.81 V)	$IrCl_6^{3-}$	0.50	0.87[f]	5.36[n]	−1.02	0.23	1.0×10^2	−0.77
	$Fe(CN)_6^{4-}$	0.50	0.36[g]	4.85[o]	7.7	0.51	1.9×10^6	−0.19
	$Fe(Me_4phen)_3^{2+}$	0.50	0.895[h]	8.5[p]	−1.45	0.34	1.2×10^3	−1.35
	$Fe(Me_2bipy)_3^{2+}$	0.50	0.94[h]	8.5[p]	−2.21	0.34	1.5×10^3[v]	−0.51
	$Fe(Me_2phen)_3^{2+}$	0.50	0.99[i]	8.5[p]	−3.06	0.34	8.8×10^2[v]	−0.06
Cr(V)[e] (E 0.72 V)	$IrCl_6^{3-}$	0.50	0.87	5.36	−2.55	0.029	1.7×10^{-2}	−6.90
	$Fe(CN)_6^{4-}$	0.20	0.36	4.85	6.1	0.23	1.3×10^2	−6.41
	$Fe(Me_4phen)_3^{2+}$	0.20	0.895	8.5	−2.98	1.04	3.4	−6.43
	$Fe(Me_2bipy)_3^{2+}$	0.50	0.94	8.5	−3.74	0.75	14	−4.00
	$Ru(NH_3)_6^{2+}$	0.20	0.067[j]	3.63[q]	11.1	1.65	$\geqslant 1 \times 10^5$	$\geqslant -6.6$
VO^{2+} (E° −0.04 V)[m]	$Co(sep)^{2+}$	1.10	−0.30[k]	0.71[r]	10.9	0.026	0.33	−6.01
	Cob(I)alamin	0.20	−0.61[l]	4.8[s]	16.2	0.99	130[t]	−9.43
	$Ru(NH_3)_6^{2+}$	1.00	0.067	3.63	4.6	0.018	1.9×10^{-3}	−7.31
$IrCl_6^{2-}$ (E° 0.87 V)[f]	$V(OH)^{2+}$	1.00	0.17	5.36	11.9	1.63	2.5×10^4	−10.2

[a] Reported electron self-exchange rate refers to reductant coreagent except for reactions of $V(OH)^{2+}$.

[b] LogK_{12} for the "cross-reaction" evaluated as $(E^\circ_{ox} - E^\circ_{red})/0.059$.

[c] Sum of electrostatic work terms, evaluated from eqn. (55).

[d] Self-exchange rate for Cr or V system, estimated from eqn. (54).

[e] Reactions were carried out in buffers of 2-ethyl-2-hydroxybutanoic acid and its anion. The Cr(V) compound was bis(chelate) 1 ($R_1{\equiv}R_2{\equiv}C_2H_5$). Values of E° have been adjusted to accommodate differences in proton numbers between oxidized and reduced forms (see Scheme 1 and ref. 77).

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barrier to electron self-exchange, which largely reflects the difference in bond lengths for the reduced and oxidized forms [79], is not greatly different for these systems and that there are no major structural alterations attending interconversion of the principal Cr(III) and Cr(IV) species. The implication is that both oxidation states are hexacovalent when chelated with the anions of α-hydroxy acids and hence that the predominant Cr(IV) species in this medium is the dihydroxo complex **11** rather than the oxo complex **10**.

In addition, the pink chelate-stabilized Cr(IV) complex, in contrast with the aquachromium(IV) cation described by Scott et al. [13], has been found not to react perceptibly with the "oxo acceptor" reagents triphenylphosphine, Sb(III) and $H_2AsO_3^-$ and the CH_3S-substituted amino acid methionine, likewise indicating that the oxo function is not present in this Cr(IV) chelate [55].

Rate constants for oxidations by Cr(V) are consistent with a k_{11} value of $10^{-6.1\pm0.8}$ for Cr(V/IV), *some five orders of magnitude below that for Cr(IV/III)* and well below the range taken to be typical of interconversions of octahedral aqua species. It is difficult to say how much of this greater barrier to self-exchange may be attributed to differing coordination numbers of the two states and how much to the stretching of the Cr=O bond in Cr(V) (structure **1**) during conversion to a Cr–O bond in Cr(IV) (**11**), but both factors may be assumed to contribute.

Comparison with the systems $V^{IV/III}$ and $V^{V/IV}$ as aqua ions (in the absence of chelating ligands) is instructive. Rate constants for oxidation by VO^{2+} (yielding $V(H_2O)_6^{3+}$) are notably low. After adjustment for differences in proton count [77], cross-reaction data in Table 4 yield a k_{11} value of $10^{-7.6\pm1.4}$ M^{-1} s^{-1} applicable to the self-exchange $[V^{IV}O(H_2O)_4]^{2+} + e^- \rightarrow [V^{III}(OH)_2(H_2O)_3]^+$ [55]. This is one of the lowest rates reported for a pair of transition metal centers and lies far beneath the reported experimental exchange rate [80]. However, the monomial inverse $[H^+]$ kinetic dependence reported for this self-exchange, in conjunction with the recognized substitution-labile character of both states, indicates that the observed self-exchange rate pertains to a process which is nearly completely inner sphere.

Maccartney [77] has estimated a V(V/IV) rate pertaining to the couple $[VO(OH)]^{2+/+}$ in the range 10^{-3}–10^{-1} M^{-1} s^{-1}. Contrast between this and the much slower V(IV/III) exchange may then be attributed, at least in part, to the presence of oxovanadium linkages in both V(V) and V(IV) but not in V(III). The calculated self-exchange rates thus indicate that the redox series V(V/IV/III) (aquated) differs from Cr(V/IV/III) (chelated) in that the major structural change in the former is associated with its 4+/3+ component whereas that in the chromium series is associated with 5+/4+.

In a sense the latter conclusion is in accord with the suggestion made some 30 years ago by Espenson and King [3a,81] pertaining to the successive $1e^-$ changes in the reduction of Cr(VI) to Cr(III) in aqueous media at low pH. However, Scott et al.'s evidence [71] that Cr(IV) in aqua systems is an oxo species, as are Cr(VI) and (presumably) Cr(V), suggests that this proposal does not apply to the conversions for which it was intended. Somewhat paradoxically, however, it appears to be valid for the chromium series in α-hydroxy acid buffers, where the intervening states which existed only transiently in the earlier work have been substantially stabilized by chelation.

8. FINAL REMARKS

In considering even the limited roster of reported Cr(IV) species [11–17], one is struck by the diversity of coordination geometry associated with this state, in marked contrast with its much more familiar tripositive counterpart which only rarely is involved in non-octahedral coordination [82]. Porphyrin derivatives of Cr(IV) are reported to be pentacovalent and to feature an oxochromium unit $Cr^{IV}(=O)$ [83], and it has been proposed [13,71] that the aqua cation of Cr(IV) has a closely related structure (although the presence of a sixth ligand has not been ruled out). Chromium(IV) in diperoxo complexes (e.g., **2**) lies in a seven-covalent pentagonal bipyramidal coordination group [17], whereas the behavior of the chelate-stabilized derivatives of this state is seen to be consistent with octahedral coordination with a Cr(=O) function absent.

Complementing this diversity in coordination geometry is a versatility in redox behavior. Aquachromium(IV) reacts primarily as a two-unit oxidant, either by oxo transfer or by hydride extraction, although it can be induced to enter into $1e^-$ transactions under special conditions. Chelated Cr(IV), on the other hand, acts mainly as a $1e^-$ oxidant, although strong $2e^-$ reductants (e.g. Sn(II)) can transfer electrons in pairs.

Increased interest in the chelate-stabilized forms of Cr(IV) is anticipated as current workers become aware of the ease with which these may be prepared and handled.

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