

Oxidation of Transition Metal Complexes by Chromium(VI)^{1a}

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The oxidation of metal complexes (a general term including hydrated ions) by chromium(VI) was among the first inorganic "redox" reactions to be studied as to reaction mechanism. Rapid reaction techniques, particularly the stopped-flow method, have recently found considerable application in this area and are partly responsible for the renewed attention paid to inorganic Cr(VI) oxidations.

The early work was prompted by the utility of chromium(VI) in classical titrimetric analysis, an application now largely supplanted by other methods, but interest continues because of the detailed mechanistic information such studies can provide. The considerable body of information concerning the nature and stability of Cr(VI) species renders it a particularly suitable choice for studies of the details of individual reaction steps. Added to this advantage is the characteristic kinetic inertness of the Cr(III) products, which can be separated and identified.

The three-unit change in oxidation number for Cr^{VI} (+3e → Cr^{III}) contrasts with the single-electron net oxidation for most transition metal complexes Mⁿ⁺ (-1e → M⁽ⁿ⁺¹⁾⁺). Consequently, the overall reactions generally occur in a sequence of steps, and reaction rates often follow complicated kinetic expressions. The existence of one or more reaction intermediates can often be inferred from the kinetics or otherwise. The complexities often add to the difficulty in characterizing a given system experimentally, but there is a reward in that they permit a more complete formulation of the individual steps which comprise the overall net process.

Kinetic evidence for reaction intermediates can often be confirmed by their reactions with added substrates which are unreactive toward the reactants and products in the time periods under consideration. Such experiments have enabled detection of Cr(V) and Cr(IV) in certain reactions. Also, it has proved possible to determine the rate laws for some Cr(V) reactions and to evaluate their relative rates. In the mechanisms considered, Cr(V) is both oxidized and reduced, in different steps, and its relative reactivity toward such alternatives also can be evaluated.

The transformation of Cr(VI), of which HCrO₄⁻ is the predominant species in dilute, acidic, aqueous solution, to Cr(III), which is produced as the octahedral

complex, Cr(H₂O)₆³⁺, in most of the reactions considered here, converts an oxoanion to a hydrated cation. The net reactions thus consume hydrogen ions. Consequently, it is not surprising that many of the reaction rates increase with hydrogen ion concentration. Edwards² has summarized observations on a large number of oxoanion reactions, noting that the rates of such reactions usually are accelerated by hydrogen ions. Some success has been realized in resolving the [H⁺] dependence of the individual steps of Cr(VI) reactions, to understand what roles protons play in the mechanism, to learn which Cr(VI) and Cr(V) species react in particular processes, and perhaps to infer something of the nature of the chromium intermediates.

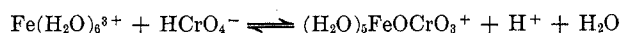
Formation of chromic acid esters is well documented; studies have identified the 1:1 complexes or condensates formed with anions (eq 1). For example, esters de-



rived from X⁻ = Cl⁻, CH₃COO⁻, and H₂PO₄⁻, as well as Cr₂O₇²⁻, the self-condensate of hydrogen chromate ion, are known.^{3,4}

Convincing arguments that the oxidation of alcohols proceeds *via* formation of esters of chromic acid have been advanced by Westheimer and coworkers.^{5,6} Similar proposals have recently been advanced to account for the mechanism of oxidation of nonmetal oxoanions such as sulfite, phosphite, and hypophosphite ions.^{7,8}

In the oxidation of metal complexes, the analog to the ester mechanism would be the inner-sphere complexation of chromate ion, followed by the reduction of coordinated Cr(VI). Chromate is known to form complexes with metal ions,⁹ *e.g.*, with Fe³⁺ as in



Complexes such as this are usually rather unstable,

(2) (a) J. O. Edwards, *Chem. Rev.*, **50**, 455 (1952); (b) "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964, pp 137-152.

(3) J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **75**, 6180 (1953).

(4) (a) G. P. Haight, Jr., D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, **3**, 1777 (1964); (b) S. A. Frennesson, J. K. Beattie, and G. P. Haight, Jr., *J. Amer. Chem. Soc.*, **90**, 6018 (1968).

(5) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

(6) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); see also J. Roček, *Collect. Czech. Chem. Commun.*, **25**, 1052 (1960), and K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, pp 159-170.

(7) G. P. Haight, Jr., F. Smentowski, M. Rose, and C. Heller, *J. Amer. Chem. Soc.*, **90**, 6324 (1968).

(8) G. P. Haight, Jr., M. Rose, and J. Preer, *ibid.*, **90**, 4809 (1968).

(9) J. H. Espenson and E. L. King, *ibid.*, **85**, 3328 (1963).

(1) (a) Work performed under the auspices of the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2765; (b) Fellow of the Alfred P. Sloan Foundation, 1968-1970.

Table I
Rate Expressions and Rate Constants for HCrO_4^- Oxidations^a

Red, Ox	n	$n + m$	$k_1, M^{-(n+1)}$ sec ⁻¹	$k_1 k_2 / k_{-1}$, $M^{-(n+m+1)}$ sec ⁻¹	Ionic strength, M	Ref
$\text{Fe}^{2+}, \text{Fe}^{3+}$	2	3	$3 \times 10^8 (0^\circ)$	$2.1 \times 10^8 (0^\circ)^b$	0.084	9
		3		$2.3 \times 10^8 (20^\circ)$	1.00	11
$\text{VO}^{2+}, \text{VO}_2^+$	0	0 ^c	$1.8 \times 10^2 (25^\circ)$	$0.56 (25^\circ)^c$	1.00	12a
$\text{V}^{3+}, \text{VO}_2^+$	0	-1	$3.9 \times 10^2 (25^\circ)$	$6 \times 10^{10} (25^\circ)^d$	1.00	13
$\text{NpO}_2^+, \text{NpO}_2^{2+}$	2	4	$7.6 (25^\circ)$	$6.1 (25^\circ)$	2.00	14
$\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Fe}(\text{C}_5\text{H}_5)_2^+$	1		$6.8 \times 10^3 (25^\circ)^e$		1.00	15
$(\text{Ta}_6\text{Br}_{12})^{2+}$, $(\text{Ta}_6\text{Br}_{12})^{3+}$	1		$3.1 \times 10^3 (25^\circ)$		1.00	16

^a $-d[\text{HCrO}_4^-]/dt = k_1[\text{Red}][\text{HCrO}_4^-][\text{H}^+]^n / (1 + k_{-1}[\text{Ox}]/k_2[\text{Red}][\text{H}^+]^m)$. ^b The value is $3.7 \times 10^8 M^{-4} \text{sec}^{-1}$ at 0° and ionic strength 0.20 M .⁹ ^c The value is $4.7 M^{-1} \text{sec}^{-1}$ at 21.1° , 1.0 M H^+ , and $\mu = 2.0 M$; $n + m$ approaches 1 at $[\text{H}^+] \sim 1 M$.^{12b} ^d Calculated from k_1 , relative values of the induced oxidation of iodide ion, and E° values. ^e In 50 vol % acetone-water; all other entries are for aqueous solution with perchlorate salts.

Table II
Rate Expressions with a Second-Order Dependence on $[\text{HCrO}_4^-]$

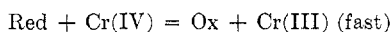
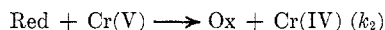
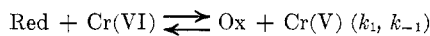
Red	Rate law term, ^a $-d[\text{HCrO}_4^-]/dt$	Rate constant
Fe^{2+}	$k''[\text{Fe}^{2+}]^2[\text{HCrO}_4^-]^2/[\text{Fe}^{3+}]$	$7 \times 10^{11} M^{-2} \text{sec}^{-1} (0^\circ)^b$
VO_2^+	$k''[\text{VO}_2^+]^2[\text{HCrO}_4^-]^2/[\text{VO}_3^+]$	$5.4 \times 10^4 M^{-3} \text{sec}^{-1} (25^\circ)^c$
$(\text{Ta}_6\text{Br}_{12})^{2+}$	$k''[(\text{Ta}_6\text{Br}_{12})^{2+}]^2[\text{HCrO}_4^-]^2[\text{H}^+]$	$3.8 \times 10^7 M^{-3} \text{sec}^{-1} (25^\circ)^d$

^a The rate constants in terms of $[\text{Cr}_2\text{O}_7^{2-}]$ are computed by multiplication of the value of k'' given by $98 M^{-1}$. ^b At $[\text{H}^+] = 0.024 M$; the variation of k'' with acid concentration was not studied.⁹ ^c Reference 12a. ^d Reference 16.

however, especially in acidic solution ($K = 0.43$ at 25.0° , $\mu = 1.0 M$).¹⁰ No direct evidence establishes that a step such as this occurs prior to oxidation, although proposals to this effect have been offered for certain metal complexes.

Many, if not all, of the reactions to be considered here proceed through a sequence of three 1-equiv steps. Scheme I generalizes this mechanism, with "Red" and "Ox" representing the respective reduced and oxidized forms of a metal complex, related by a single electron transformation: $\text{Ox} + e^- \rightleftharpoons \text{Red}$. Only the first two steps have been found to be important rate steps in the cases encountered to date. Scheme I

Scheme I



leads to the following steady-state rate law

$$\frac{-d[\text{Cr(VI)}]}{dt} = \frac{k_1 k_2 [\text{Cr(VI)}][\text{Red}]^2}{k_2 [\text{Red}] + k_{-1} [\text{Ox}]} \quad (2)$$

Certain of the reactions contain an additional kinetic term dependent upon $[\text{HCrO}_4^-]^2$, which probably represents the parallel oxidation by $\text{Cr}_2\text{O}_7^{2-}$, although this is not a unique interpretation.

Tables I^{9,11-16} and II^{9,12a,16} summarize the complete

(10) J. H. Espenson and S. R. Helzer, *Inorg. Chem.*, **8**, 1051 (1969).

(11) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 2887 (1969).

(12) (a) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 1883, 5101 (1964); (b) D. R. Rosseinsky and M. J. Nicol, *J. Chem. Soc. A*, 1196 (1970).

(13) K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, **92**, 1884 (1970).

(14) J. C. Sullivan, *ibid.*, **87**, 1495 (1965).

(15) J. R. Pladziewicz and J. H. Espenson, manuscript in preparation.

kinetic information, as available at present, for the reactions under consideration. In a given section of the following discussion of these reactions, attention may be focused on a particular rate term, or upon one limiting form of a more general equation.

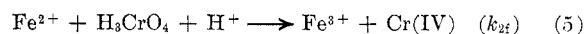
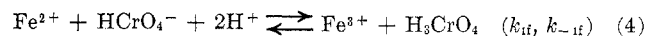
This Account sets forth the basic kinetic and mechanistic information, organized as follows: (1) the reactions exhibiting a first-order dependence on $[\text{HCrO}_4^-]$, first hydrated metal ions and then other complexes, (2) mechanisms other than Scheme I, (3) the interpretation of the second-order HCrO_4^- terms, (4) the reactions and properties of Cr(V) and Cr(IV), and (5) some thermodynamic and structural aspects of the mechanisms.

The Oxidation of Hydrated Metal Ions

$\text{Fe}(\text{H}_2\text{O})_6^{2+}$. Considerable study has been devoted to this reaction using a variety of experimental methods and covering wide concentration ranges.^{5,9,11,17,18} Under many conditions the kinetic data conform to the expression¹⁹

$$\frac{-d[\text{HCrO}_4^-]}{dt} = \frac{k_i [\text{Fe}^{2+}]^2 [\text{HCrO}_4^-] [\text{H}^+]^3}{[\text{Fe}^{3+}] + k_i' [\text{Fe}^{2+}] [\text{H}^+]} \quad (3)$$

This result is consistent with Scheme I, with the elementary reactions 4 and 5, where $k_i = k_{1f} k_{2f} / k_{-1f}$ and



(16) J. H. Espenson and R. J. Kinney, *Inorg. Chem.*, in press.

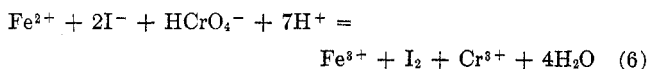
(17) C. Benson, *J. Phys. Chem.*, **7**, 1, 356 (1903).

(18) J. H. Espenson, *J. Amer. Chem. Soc.*, **92**, 1880 (1970).

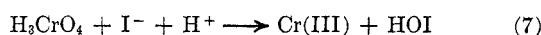
(19) Here and elsewhere other pathways or limiting forms may be neglected for the purpose at hand; this is only the part of the rate expression corresponding to the pathway with a first-order dependence on $[\text{HCrO}_4^-]$. See Tables I and II.

$k_f' = k_{2f}/k_{-1f}$, assuming steady-state behavior for the intermediates. The formula given for Cr(V) is, naturally, arbitrary to the extent of the number of solvent molecules, *i.e.*, $H_3CrO_4 \pm nH_2O$, and the formula is not intended to imply particular oxo or hydroxo or aquo coordination to Cr(V), although arguments will later be presented for four-coordinate Cr(V).

The oxidation of iodide ions is induced by this reaction. (Neither Fe^{3+} nor $HCrO_4^-$ oxidizes I^- rapidly, but Cr(V) does.) In the limit of a high ratio of $[I^-]$ to $[Fe^{2+}]$, where Cr(V) reacts predominantly with I^- , the stoichiometry becomes



The limiting value of 2.0 for the induction factor,²⁰ F_i (= moles of I^- oxidized/moles of Fe^{2+} oxidized) confirms that the substance responsible for the oxidation of I^- is Cr(V).⁵ Because F_i is independent of $[H^+]$, the elementary reaction for I^- oxidation by Cr(V) is



$V(H_2O)_6^{3+}$ and VO^{2+} . These two oxidations constitute distinct processes when studied separately, the conversion of V^{3+} to VO^{2+} being complete before substantial oxidation of VO^{2+} to VO_2^+ has occurred. The oxidation of V^{3+} is, however, catalyzed by higher concentrations of VO^{2+} , which leads to interdependent mechanisms.

First, in the individual reactions, the oxidation of V^{3+} by $HCrO_4^-$ is given by the rate law 8,¹³ whereas

$$-d[HCrO_4^-]/dt = k_r[V^{3+}][HCrO_4^-] \quad (8)$$

the rate of the VO^{2+} reaction is¹²

$$\frac{-d[HCrO_4^-]}{dt} = k_v \frac{[VO^{2+}]^2[HCrO_4^-]}{[VO_2^+]} \quad (9)$$

The distinction between these two kinetic forms is illustrated in Figure 1. Both rate expressions are consistent with the general mechanism in Scheme I; the rate constant of eq 8 is identified as k_{1r} , and k_v in eq 9 is $k_{1v}k_{2v}/k_{-1v}$.²¹ In the latter case, the Cr(V) \rightarrow Cr(IV) step is the slowest, and inequality 10 reduces the

$$k_{-1v}[VO_2^+] \gg k_{2v}[VO^{2+}] \quad (10)$$

general expression to the limiting form of eq 9.

To summarize a number of important features: (1) both rate constants are independent of $[H^+]$,^{12,13,22} (2) the V^{3+} rate is not affected by small concentrations of VO^{2+} , say $\leq 0.1[V^{3+}]$, (3) the oxidation of V^{3+} produces no VO_2^+ directly, eliminating two-electron steps at any stage of the reaction, (4) both reactions

(20) C. Wagner and W. Preiss, *Z. Anorg. Allg. Chem.*, **168**, 265 (1928).

(21) To facilitate later discussion the parameters of Scheme I will be designated by the subscripts *f* (Fe^{2+}), *r* (V^{3+}), *v* (VO^{2+}), and *n* (NpO_2^+).

(22) After correction¹³ for the protonation equilibrium $H_3CrO_4 \rightleftharpoons HCrO_4^- + H^+$. Recent work^{12b} has indicated an additional term with a first-order dependence on $[H^+]$ becomes important at higher $[H^+]$ than originally studied.^{12a}

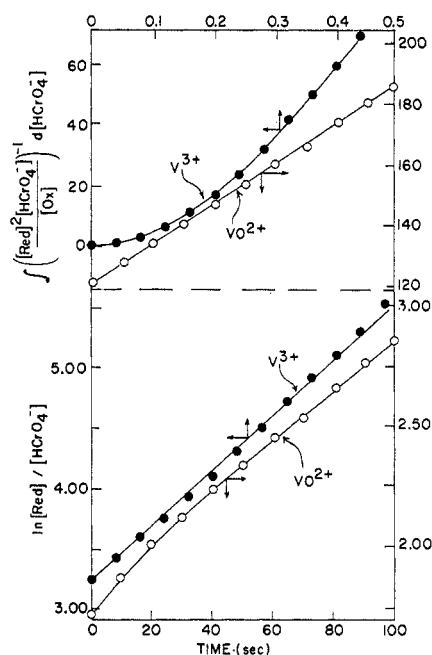
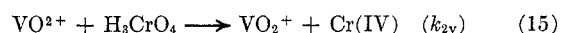
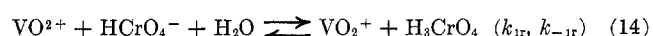
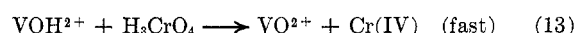
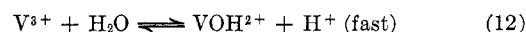
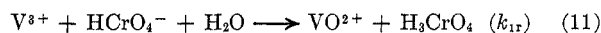


Figure 1. Illustrating the different rate expressions for the oxidation of VO^{2+} (open circles) and V^{3+} (filled circles) by $HCrO_4^-$. The data are from ref 13 (V^{3+}) and 12 (VO^{2+}). The integral in the upper part of the figure was computed according to eq 9 of ref 9.

induce the oxidation of iodide ion,^{12a,13,23} with a limiting value of 2.0 for F_i as depicted in Figure 2, (5) F_i depends upon $[H^+]$, as evaluated for the oxidation of both V^{3+} and VO^{2+} , and (6) the oxidation of VO^{2+} shows the inverse dependence on $[VO_2^+]$ as in eq 9, even when VO_2^+ is not added initially, such that inequality 10 becomes valid within the first 1–3% of reaction.²⁴

The following elementary reactions apply to the V^{3+} reaction (eq 11–13) and to the VO^{2+} reaction (eq 14 and 15).



The oxidation of mixtures²⁵ of V^{3+} and VO^{2+} affords a value for k_{1v} of eq 14, using the reaction of V^{3+} and VO_2^+ (eq 16). This occurs very rapidly²⁶ under the



conditions of interest (0.005–0.1 M H^+), keeping $[VO_2^+]$ very small, so that eq 10 no longer applies. In effect, VO_2^+ catalyzes the V^{3+} – $HCrO_4^-$ reaction by generating

(23) R. Luther and T. F. Rutter, *Z. Anorg. Chem.*, **54**, 1 (1907).

(24) Were Rosseinsky and Nicol's suggestion that "a pathway first-order in vanadium(IV) is to be expected at very low $[V(IV)]$ " (ref 12b) to be realized, it would necessarily represent a mechanism totally independent of Scheme I, for which the limiting form $k_1[VO^{2+}][HCrO_4^-]$ is revealed at a high $[V(IV)]/[V(V)]$ ratio (ref 25 and eq 2).

(25) K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, **92**, 1889 (1970).

(26) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **68**, 612 (1964).

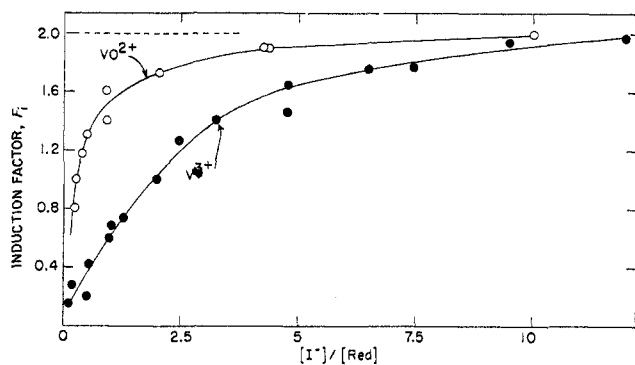


Figure 2. The oxidation of iodide ions induced by the VO_2^+ - HCrO_4^- reaction at $0.0050 M \text{H}^+$ (open circles) and by the V^{3+} - HCrO_4^- reaction at $0.0200 M \text{H}^+$ (filled circles), as a function of $[\text{I}^-]/[\text{Red}]$. F_1 is the ratio of the moles of iodide oxidized to the moles of Red oxidized (data from ref 12 and 13).

Cr(V) in reaction 14. The overall rate is given by

$$-d[\text{HCrO}_4^-]/dt = k_{1r}[\text{V}^{3+}][\text{HCrO}_4^-] + k_{1v}[\text{VO}_2^+][\text{HCrO}_4^-] \quad (17)$$

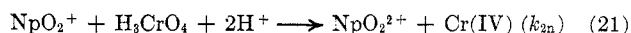
Figure 3 depicts the effect of VO_2^+ , from which the otherwise inaccessible k_{1v} can be evaluated. It is this study of the composite V^{3+} - VO_2^+ reaction that permits further resolution of the kinetic data in eq 9 into the mechanism of eq 14-15, particularly with regard to protonation.

NpO_2^+ . The oxidation of NpO_2^+ to NpO_2^{2+} occurs according to reaction 18, whose rate is given by $3\text{NpO}_2^+ + \text{HCrO}_4^- + 7\text{H}^+ = 3\text{NpO}_2^{2+} + \text{Cr}^{3+} + 4\text{H}_2\text{O}$ (18) eq 19.¹⁴ This result is in accord with Scheme I, with

$$\frac{-d[\text{HCrO}_4^-]}{dt} = \frac{k_n[\text{NpO}_2^+]^2[\text{HCrO}_4^-][\text{H}^+]^4}{[\text{NpO}_2^{2+}] + k_n'[\text{NpO}_2^+][\text{H}^+]^2} \quad (19)$$

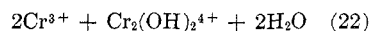
the elementary reactions 20 and 21, where $k_n = \text{NpO}_2^+ + \text{HCrO}_4^- + 2\text{H}^+ + \rightleftharpoons \text{NpO}_2^{2+} + \text{H}_3\text{CrO}_4$

$$(k_{1n}, k_{-1n}) \quad (20)$$

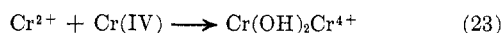


$k_{1n}k_{2n}/k_{-1n}$ and $k_n' = k_{2n}/k_{-1n}$.

$\text{Cr}(\text{H}_2\text{O})_6^{3+}$. The oxidation of Cr^{2+} by HCrO_4^- , although too rapid for kinetic study, has been considered mechanistically.^{27,28} Only ca. 50% of the Cr(III) product is $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, the remainder being $\text{Cr}_2(\text{OH})_2^{4+}$, a hydroxo-bridged binuclear ion.²⁹ The net equation is thus (22), suggesting the familiar three-step pattern of $3\text{Cr}^{2+} + \text{HCrO}_4^- + 5\text{H}^+ =$



Scheme I, the last step being responsible for the dinuclear product (eq 23). Reaction 23 is known in-



dependently,²⁷ which affirms the proposed mechanism.

The basic features outlined above were confirmed by a ^{51}Cr ($^*\text{Cr}$) tracer study at relatively high and equiva-

(27) M. Ardon and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3197 (1959).

(28) L. S. Hegeudus and A. Haim, *Inorg. Chem.*, **6**, 664 (1967).

(29) R. W. Kolaczowski and R. A. Plane, *ibid.*, **3**, 322 (1964).

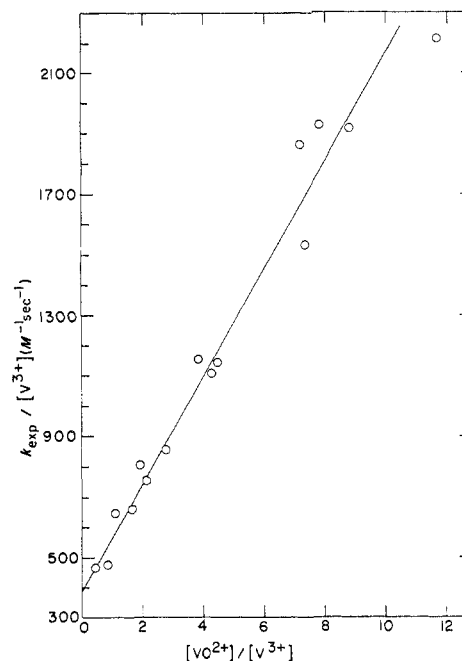
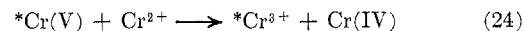
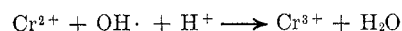
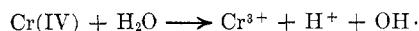


Figure 3. Linear dependence of the apparent second-order rate constant for the reaction of V^{3+} and HCrO_4^- as a function of the concentration ratio $[\text{VO}_2^+]/[\text{V}^{3+}]$, according to eq 17 (data from ref 25).

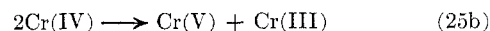
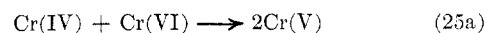
lent concentrations ($0.01 M$).²⁸ It was, however, noted that small and reproducible quantities of $^*\text{Cr}^{3+}$ resulted from $\text{Cr}^{2+} + \text{H}^*\text{CrO}_4^-$, implicating an important side reaction, suggested to be the two-electron reaction 24. At much lower concentrations and with



Cr(VI) in excess, King, *et al.*,³⁰ found a considerably smaller ratio of $\text{Cr}_2(\text{OH})_2^{4+}/\text{Cr}^{3+}$. They suggest that the following steps may compete with eq 23 under conditions of excess Cr(VI).



Alternatively, one of the reactions 25 might constitute



the source of the deviation,³¹ because the Cr(V) could perhaps undergo reactions producing Cr^{3+} in preference to the binuclear ion.

$\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Electron exchange between Cr^{3+} and HCrO_4^- takes place very slowly.³² Elevated temperatures, high concentrations, and extended reaction times are required to establish isotopic equilibrium. The rate expression involves fractional exponents (eq 26).

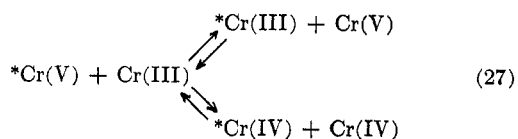
$$R_{\text{ex}} = k_{\text{ex}}[\text{Cr}(\text{H}_2\text{O})_6^{3+}]^{4/3}[\text{HCrO}_4^-]^{2/3} \quad (26)$$

(30) A. C. Adams, J. R. Crook, F. Bockhoff, and E. L. King, *J. Amer. Chem. Soc.*, **90**, 5761 (1968).

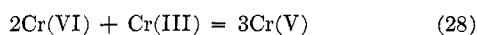
(31) This possibility originated from suggestions made by Professor G. P. Haight, Jr., to the author. Haight (unpublished experiments) has found that reaction 25b is needed to explain the effect of Mn^{2+} on the rate and stoichiometry of the oxidation of N_2H_4 by Cr(VI).

(32) C. Altman and E. L. King, *J. Amer. Chem. Soc.*, **83**, 2825 (1961).

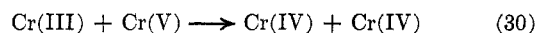
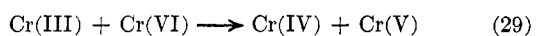
Despite its apparent complexity, the rate law is consistent with a single rate-determining reaction, which may be one of the following.



The steady-state concentration of Cr(V) is fixed by equilibrium 28, which is suggested²² to proceed by the



mechanism 29, 30. These results and others suggest



relatively rapid electron exchange between the pairs Cr(VI)–Cr(V) and Cr(IV)–Cr(III). The latter reaction occurs more slowly than the reduction of Cr(IV) by Cr²⁺ (eq 23), however, otherwise the tracer experiments on the Cr²⁺–HCrO₄[–] reaction would not have been possible.

The Oxidation of Other Metal Complexes

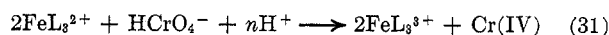
Fe(CN)₆^{4–}, Fe(CN)₄(bipy)^{2–}, and Fe(CN)₂(bipy)₂. The rate expressions for these reactions³³ are consistent with the general three-step mechanism shown in Scheme I. Protolytic equilibria complicate the kinetic expressions, especially for Fe(CN)₆^{4–}. The first step in the oxidation sequence is rate determining under all the conditions studied. The reactants were consumed in the expected ratio, 3Fe(II)/1Cr(VI), but only *ca.* 2/3 of the anticipated amount of the corresponding Fe(III) complex was formed, the remainder being accounted for as a dinuclear complex of Cr(III) and Fe(III). Elemental analyses on the fraction of product solutions which was retained neither by cation- nor anion-exchange resin suggest (H₂O)₅CrNCFe(CN)₅ is the product of the first reaction. The elution characteristics exhibited during ion-exchange chromatography suggested CrNCFe(bipy)(CN)₃²⁺ and CrNCFe(bipy)₂(CN)₄⁺ were formed in the other reactions. In agreement with this, Cr(H₂O)₆³⁺ was not found in the experiments with any of these complexes.

It appears all three of these dinuclear complexes are formed during the third step of the overall reaction. Reduction of Cr(IV) by each of the iron(II) complexes occurs *via* an inner-sphere electron-transfer process using CN[–] as a bridging anion for electron transfer.

Fe(phen)₃²⁺ and Fe(bipy)₃²⁺. Much of the reaction of both complexes proceeds by a kinetic term having the form $k_1[\text{FeL}_3^{2+}][\text{HCrO}_4^-]$, with k_1 showing one or more H⁺-dependent terms.^{9, 33} These findings are in accord with Scheme I, with the first of the three steps the slowest.

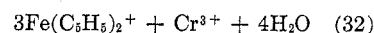
Not accounted for by those reactions are apparent deviations that can be reconciled, at least empirically, with terms containing a second-order dependence on

[FeL₃²⁺]. This path may reflect a two-electron pathway giving Cr(IV) directly (eq 31). Alternatively,



the higher order term may merely represent the consequence of the acid hydrolysis of the iron(III) complex, at least for Fe(bipy)₃²⁺.^{33, 34}

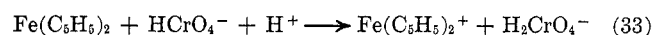
Fe(C₅H₅)₂. The oxidation of ferrocene¹⁵ in acetone-water proceeds according to reaction 32 with apparent



oxidation beyond Fe(C₅H₅)₂⁺ with excess Cr(VI) over longer times. The main reaction follows the rate expression

$$-d[\text{HCrO}_4^-]/dt = k[\text{Fe(C}_5\text{H}_5)_2][\text{HCrO}_4^-][\text{H}^+]$$

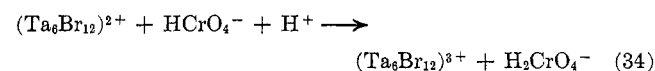
suggesting the elementary reaction 33.



(Ta₆Br₁₂)²⁺. The oxidation of the 2+ tantalum cluster ion produces (Ta₆Br₁₂)³⁺; only after longer times with excess Cr(VI) is (Ta₆Br₁₂)⁴⁺ produced, and that reaction may be accompanied by some decomposition of the cluster ion. The rate in dilute aqueous perchloric acid is given by¹⁶

$$-d[\text{HCrO}_4^-]/dt = k[(\text{Ta}_6\text{Br}_{12})^{2+}][\text{HCrO}_4^-][\text{H}^+]$$

and the proposed elementary reaction is



Oxidations of Cr(H₂O)₆³⁺. It is appropriate to consider reactions in which Cr³⁺ is oxidized to HCrO₄[–], as the mechanisms may involve the same steps. The oxidation of Cr³⁺ by Ce(IV)–sulfate complexes³⁵ follows the rate law

$$\frac{d[\text{HCrO}_4^-]}{dt} = k \frac{[\text{Ce(IV)}]^2[\text{Cr}^{3+}]}{[\text{Ce(III)}]}$$

This result suggests a mechanism as shown in Scheme I (in reverse), with $k = k_{-2}k_{-2}/k_3$. The oxidation of Cr³⁺ by Ag²⁺ follows a second-order rate expression,³⁶ $k[\text{Ag}^{2+}][\text{Cr}^{3+}]$. This may represent the first step of a similar sequence, as has been proposed, although no more direct evidence is available.

Other Possible Mechanisms

Alternatives to Scheme I and related reactions (*e.g.*, eq 25) are mechanisms for the oxidation of Red to Ox such as Schemes II and III (where Ox⁺ is the double oxidized species Ox⁺ ⇌ Ox ⇌ Red).

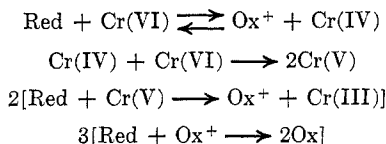
The reaction kinetics eliminate either possibility for the reactions of Fe²⁺, VO²⁺, Ce(IV), and NpO₂⁺. For the V³⁺ reaction, experiments were done at high [H⁺] where the step Red + Ox⁺ → 2Ox (namely

(34) The kinetic data³³ for Fe(bipy)₃²⁺ were rather poorly reproducible, perhaps due to this decomposition reaction.

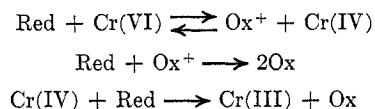
(35) J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **82**, 3805 (1960).

(36) J. B. Kirwin, P. J. Proll, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **60**, 119 (1964).

Scheme II

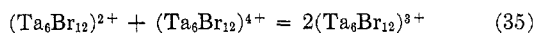


Scheme III

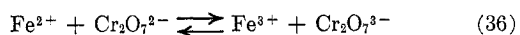


$\text{V}^{3+} + \text{VO}_2^+ \rightarrow 2\text{VO}^{2+}$) occurs slowly. No VO_2^+ was detected, eliminating Schemes II and III, along with any other mechanism incorporating a two-electron oxidation of V^{3+} by the main reactant or by intermediates.

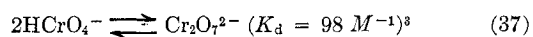
For the remainder of the reactions, where the rate expression basically takes the form $k[\text{Red}][\text{Cr(VI)}]$, any of the three mechanisms is possible (as, of course, are a number of other kinetically equivalent mechanisms). Because of the other similarities it seems probable that the mechanisms are the same. It would, however, be premature to reject other possibilities such as Scheme III, particularly in a case such as the oxidation of $(\text{Ta}_6\text{Br}_{12})^{2+}$, which is easily³⁷ oxidized to $(\text{Ta}_6\text{Br}_{12})^{4+}$, for which the necessary subsequent reaction (eq 35) occurs rapidly.³⁸

Rate Terms Dependent on $[\text{HCrO}_4^-]^2$

Westheimer⁵ has proposed a direct reduction of $\text{Cr}_2\text{O}_7^{2-}$ in the case of Fe^{2+} ,³⁹ where a parallel rate term in $[\text{HCrO}_4^-]^2$ was noted¹¹ (eq 36). The $[\text{HCrO}_4^-]$



dependence is accounted for by the known equilibrium 37. A term of this form was found for VO^{2+} , Fe -



$(\text{C}_5\text{H}_5)_2$, and $(\text{Ta}_6\text{Br}_{12})^{2+}$, whereas it is not important pathway for NpO_2^+ , V^{3+} , and the Fe(II) -cyanide complexes. Table II summarizes the kinetic data. No reason emerges for the different patterns, but the absent term may imply only an insufficient range of $[\text{Cr(VI)}]$ variation or minor differences in the reactivity

(37) N. E. Cooke, T. Kuwana, and J. H. Espenson, submitted for publication.

(38) N. Winograd and T. Kuwana, *J. Amer. Chem. Soc.*, **92**, 224 (1970).

(39) The rate term varying with $[\text{HCrO}_4^-]^2$ is much more important in sulfate media¹⁷ than in perchlorate.⁹ Rosseinsky and Nicol¹¹ have proposed a different rate term, $b[\text{Fe}^{2+}][\text{HCrO}_4^-][\text{H}^+]$, from electrochemical studies with high $[\text{Fe}^{3+}]$ and $[\text{Cr(VI)}]$ and very low $[\text{Fe}^{2+}]$. The data⁹ on which the $[\text{HCrO}_4^-]^2$ term is based are not particularly precise, being superimposed on the larger kinetic term of eq 3. Their expression necessarily represents a pathway independent of Scheme I.²⁴ Since the deviations from the limiting form of eq 3 reached at high $[\text{Fe}^{3+}]$ are relatively small, an explanation other than a new rate term might be sought. G. P. Haight, Jr. (private communication) has noted that under the concentration extreme $[\text{Cr(VI)}] \gg [\text{Fe(II)}]$ the oxidation of Cr(IV) by Cr(VI) might compete with its reduction by Fe(II) . The additional Cr(V) so produced could account for up to a twofold increase in rate of Fe(II) oxidation.

of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ toward the different reducing agents.

The proposal regarding dichromate might be checked for a reaction occurring rapidly relative to the rate of the monomer-dimer equilibration 37, which in dilute aqueous perchloric acid solutions of pH 2-4 is given by eq 38. The rate represented by eq 38 is much higher

$$d[\text{Cr}_2\text{O}_7^{2-}]/dt = k_2[\text{HCrO}_4^-]^2[\text{H}^+] - k_1[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+] \quad (38)$$

$$k_2 = 6.2 \times 10^5 \text{ M}^{-2} \text{ sec}^{-1}, k_1 = 6.3 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}{}^{40}$$

than that for metal complexes under the conditions studied, preventing, as yet, confirmation of this point.

Intermediate Oxidation States of Chromium

Compounds of both Cr(V) and Cr(IV) have been prepared, although they are not common. Solutions of Cr(VI) in very concentrated KOH liberate oxygen on heating, generating a green Cr(V) species, presumably CrO_4^{3-} , which is unstable to water or oxygen. The existence of Cr(V) in this preparation has been confirmed by esr spectroscopy.⁴¹ Wiberg and Schäfer have detected sizable concentrations of Cr(V) in 97% acetic acid, where it is rather slow to decompose, and have reported its electronic and esr spectra.⁴² The best evidence for Cr(V) in acidic aqueous reaction systems remains the scavenging experiments, particularly those with iodide ions.

The Cr(V) species H_3CrO_4 was produced⁴³ in most of the reactions, *e.g.*, in eq 4, 11, 14, and 20, although in at least two other reactions, eq 33 and 34, the Cr(V) species was H_2CrO_4^- . The different elementary reactions do not need to produce the species of Cr(V) which is the most stable protolytic form in the medium, nor must they all produce the same species. On the other hand, the fact that the species produced do not cover a wide array of protolytic possibilities supports the suggestion that the reactions have a common Cr(V) intermediate.

In some cases the form of the overall rate expression itself gives the rate law for the step involving oxidation by Cr(V) , as in eq 5, 15, and 21. The form of the V(III) - Cr(V) rate step, although not entering the overall reaction kinetics, is determined by the competition experiments with I^- ¹³

$$-d[\text{H}_3\text{CrO}_4]/dt = k_{2r}[\text{V}^{3+}][\text{H}_3\text{CrO}_4]/[\text{H}^+]$$

On this basis, the reaction of VOH^{2+} and H_3CrO_4 was proposed, as shown in eq 12 and 13 (other possibilities exist, but some support¹³ can be offered for the elementary step shown). Table III summarizes the re-

(40) J. R. Pladziewicz and J. H. Espenson, *Inorg. Chem.*, in press. The rate constants refer to 25.0°, $\mu = 1.00 \text{ M}$, in perchlorate solution.

(41) (a) N. Bailey and M. C. R. Symons, *J. Chem. Soc.*, 203 (1957); (b) A. Carrington, D. J. E. Ingram, D. S. Schonland, and M. C. R. Symons, *ibid.*, 4710 (1956).

(42) K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, **91**, 927, 933 (1969).

(43) In cases where $[\text{Ox}]$ does not enter the rate law, this conclusion is based on the assumption that the first step produces Ox in the protolytic form that predominates at equilibrium in the medium in question.

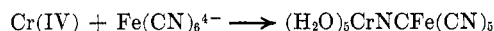
Table III
Relative Rates of Oxidations by Cr(V)

Elementary reaction	Rel rate ^a	Ref
$I^- + H_3CrO_4 + H^+ \rightarrow Cr(III) + HOI$	1.00	12a, 18, 25
$Fe^{2+} + H_3CrO_4 + H^+ \rightarrow Fe^{3+} + Cr(IV)$	0.19	18, 20
$VO^{2+} + H_3CrO_4 \rightarrow VO_2^+ + Cr(IV)$	$3.7 \times 10^{-4}/[H^+]$	12a, 25
$VOH^{2+} + H_3CrO_4 \rightarrow VO^{2+} + Cr(IV)$	$2.8 \times 10^{-4}/[H^+]^2$	13

^a The rate expression for the oxidation of V(III) is $k[V^{3+}][HCrO_4^-]/[H^+]$, and the rate constant is so defined; the bimolecular reaction written is assumed to be the actual elementary reaction (see ref 13).

activity of Cr(V) toward different reducing agents, relative to the rate of iodide oxidation.

The products obtained upon oxidation of $Fe(CN)_6^{4-}$ and related complexes suggest an inner-sphere mechanism. The binuclear product can be isolated because



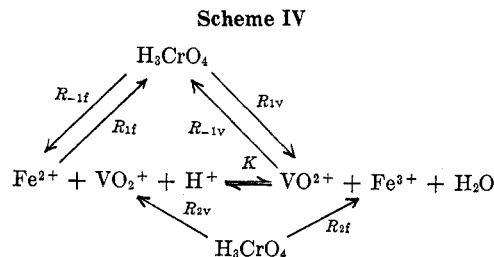
Fe(III) and Cr(III) both undergo slow ligand substitution. This mechanism requires that Cr(IV) ligand substitution be faster than its reduction, which appears to be the case.⁴⁴

Reduction of Cr(VI) in the presence of potential complexing agents for Cr(III) often results in Cr(III) complexation,⁴⁵ which is probably more common than has been recognized. Ligand capture can be interpreted in terms of the formation of a Cr(IV) complex, which is reduced to a kinetically stable Cr(III) complex, and is expected to be more important for nonmetal and oxoanion reactions than in the present case.

Thermodynamic Considerations

Certain rate and equilibrium constants are interrelated, as illustrated in Scheme IV. The check of known thermodynamic values is adequate, considering the use of determinations made under conditions of differing temperature and medium.^{12a} Also, the concentration dependences of the observed rates and of the F_1 determinations do combine to give the correct form for the equilibrium constant.

On the basis of an analogous scheme for V^{3+} , also leading to the correct equilibrium formulation, a value was calculated for the undetermined quotient k_{2r}/k_{1r} , included in Table I.



$$K = \frac{k_{1f}k_{-1v}}{k_{-1f}k_{1v}} = \left(\frac{k_{1f}k_{2f}}{k_{-1f}}\right)\left(\frac{k_I}{k_{2f}}\right)\left(\frac{k_{-1v}}{k_{1v}k_{2v}}\right)\left(\frac{k_{2v}}{k_I}\right)$$

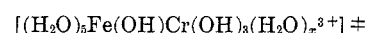
(44) A. E. Ogard and H. Taube, *J. Amer. Chem. Soc.*, **80**, 1084 (1958).

(45) (a) M. T. Beck and I. Bárdi, *Acta Chim. (Budapest)*, **29**, 3 (1961); (b) M. T. Beck, I. Seres, and I. Bárdi, *ibid.*, **41**, 231 (1964).

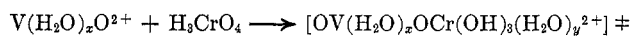
Stereochemical Aspects

Based on kinetic differences, some arguments concerning the nature of chromium coordination in the intermediates have been made.^{9, 12a, 32, 33, 35} In the reactions of those substances having suitable bridging ligands, or capable of labile ligand substitution, which includes Fe^{2+} , VO^{2+} , NpO_2^{2+} (there being fast exchange of the H_2O groups, but not of the oxo ligands), and $Ce(IV)$, either step can be rate determining. Concentration conditions needed to make the Cr(V)–Cr(IV) step the slowest are readily achieved, making it the main rate-determining process under most conditions. In contrast, the first reduction step, $Cr(VI) \rightarrow Cr(V)$, is the slowest in the case of reducing agents having slowly substituted groups, such as $Fe(CN)_6^{4-}$ and its bipyridine derivatives, $Fe(phen)_3^{2+}$, $Fe(C_5H_5)_2$, $(Ta_6Br_{12})^{2+}$, and $V(H_2O)_6^{3+}$.

These results and also the Cr(III)–Cr(VI) exchange mechanism may be related to the change in coordination number (CN) in the reduction from $HCrO_4^-$ with CN 4 to $Cr(H_2O)_6^{3+}$ with CN 6. The proposal is that the change takes place at the middle step, from Cr(V) with CN 4 to Cr(IV) with CN 6. This barrier becomes particularly pronounced for a labile reducing agent, or one possessing suitable bridging groups, as can be depicted for Fe^{2+}



The separation of the binuclear intermediate to Cr(IV) and Fe(III) generates a competition for the presumed bridging hydroxo group which tends to decrease chromium coordination in a step wherein it needs to increase. Likewise, it appears the conversion of VO^{2+} to VO_2^+ could be facilitated by an inner-sphere mechanism, but the coordination sphere of Cr would not be



expanded by this step, as needed, were the oxo bridge subsequently surrendered to vanadium.

With complexes reacting by a nonbridging mechanism, on the other hand, whatever H_2O or OH or X^- groups added to Cr during the reduction from Cr(V) to Cr(IV) can be retained, making this a more favorable process. In these cases the first step may be left as rate determining simply because, of the three, it has the least thermodynamic driving force.