Kinetics and Mechanism of the Oxidation of Vanadium(III) by Chromium(VI) in Aqueous Perchloric Acid Solutions[1a]

Keith M. Davies and James H. Espenson[1b]

Contribution from the Institute for Atomic Research and
the Department of Chemistry, Iowa State University, Ames, Iowa 50010.
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Abstract: The oxidation of V^{3+} to VO^{2+} by $HCrO_4^-$ occurs in three one-equivalent steps, the first of which is rate determining. The rate expression is $-d[HCrO_4^-]/dt = k[V^{3+}][HCrO_4^-]$, with $k = 386 \pm 14\ M^{-1}\ sec^{-1}$ at 25.0° and $\mu = 1.00\ M$, independent of $[H^+]$. The reaction does not involve a two-electron step as VO_2^+, detectable and metastable under these circumstances, was absent. The formation of VO^{2+} was also measured confirming the single-electron sequence. The oxidation of iodide ion is induced by the vanadium(III)–chromium(VI) reaction, the limiting induction factor of 2.0 providing additional evidence for a chromium(V) intermediate. From a study of the induced oxidation of iodide ion the rate expression and a rate constant for the V(III)–Cr(V) reaction relative to the I^-–Cr(V) reaction were obtained.

The oxidation of metal ions by chromium(VI) has been a subject of long-standing interest.[2] The oxidation of V(III) by Cr(VI) was referred to by Luther and Rutter,[3] who established that the reaction of V(III) with Cr(VI) in sulfuric acid solution induced the oxidation of iodide ion. They found a limiting induction factor of 2.0 (= moles of I^- oxidized/moles of V(III) oxidized), suggesting[2] that Cr(V) is an important intermediate. This now appears to be a rather general conclusion for the oxidation of metal ions by Cr(VI).

No kinetic studies on the rather rapid oxidation of V(III) by Cr(VI) have been published, however, and the present work on the reaction kinetics was undertaken to establish those features of the mechanism that can be studied by such methods. Among the issues of particular interest in this reaction are comparisons with the results of studies dealing with the Cr(VI) oxidation of iron(II)[4] and its complexes,[4a,5] neptunium(V),[6] and oxovanadium(IV).[7]

The oxidation of V^{3+} by $HCrO_4^-$ occurs at a much higher rate than does the oxidation of VO^{2+}.[7] Consequently, this second reaction can be ignored.[8,9] The net reaction can be represented by the following equation when V(III) is in excess.

$$3V^{3+} + HCrO_4^- + H^+ = 3VO^{2+} + Cr^{3+} + H_2O \qquad (I)$$

The earlier studies[2–7] on Cr(VI) oxidations of metal ions have suggested quite strongly that the reaction proceeds in three successive steps, as shown in Scheme I. For substitution-labile reducing agents (*e.g.*, Fe^{2+}, VO^{2+}) the second reduction step, Cr(V) to Cr(IV), limits the rate, whereas for substitution-inert species the initial step is the slowest. Whether these generalizations are completely valid, however, yet remains to be established. The exchange of $V(H_2O)_6^{3+}$ and solvent water may occur too slowly[10] for a ligand-bridged mechanism to be invoked here, in which case one anticipates an outer-sphere process with the initial reduction the rate determining step.

Scheme I

$$\mathrm{V(III) + Cr(VI) \rightleftarrows V(IV) + Cr(V)}$$
$$\mathrm{V(III) + Cr(V) \rightleftarrows V(IV) + Cr(IV)}$$
$$\mathrm{V(III) + Cr(IV) \rightleftarrows V(IV) + Cr(III)}$$

The scavenging effect of I^- toward Cr(V) has been demonstrated in a number of different reactions producing this intermediate in a one-electron reduction of Cr(VI).[2,3,7b,11] Such experiments not only provide a basis for possibly establishing the role of Cr(V) in the mechanism, but they also provide additional kinetic information. Applied to the present system, the study of the induced oxidation of iodide ion will measure the rate constant for the V(III)–Cr(V) rate relative to that of I^-–Cr(V). The form of the rate equation governing the V(III)–Cr(V) reaction can also be obtained since the rate law for the I^-–Cr(V) reaction is known.[7b,8] These results are particularly informative because the direct kinetic study on reaction I reveals information only on the first step of the reaction sequence if that step is rate determining throughout.

The presumption underlying the considerations set forth in the preceeding discussion is that the reaction occurs according to the mechanism shown in Scheme I. Because vanadium also exhibits a stable 5+ oxidation state, the possible occurrence of a two-electron mechanism cannot be dismissed. Owing to the low rate of reaction between V(III) and V(V)[12] at high $[H^+]$ (k =

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[1] (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2628; (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

[2] F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1948). This review contains a critical summary of the earlier literature.

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

[4] (a) J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, **85**, 3328 (1963); (b) J. H. Espenson, *ibid.*, **92**, 1880 (1970).

[5] J. P. Birk, *ibid.*, **91**, 3189 (1969).

[6] J. P. Sullivan, *ibid.*, 87, 1495 (1965).

[7] (a) J. H. Espenson, *ibid.*, **86**, 1883 (1964); (b) *ibid.*, **86**, 5101 (1964).

[8] K. M. Davies and J. H. Espenson, *ibid.*, **92**, 1889 (1970).

[9] Actually this is not strictly true; although the overall reaction between V(IV) and Cr(VI) is slow,[7] the first step has a rate constant comparable to the V(III)–Cr(VI) reaction. Because the V(III) reactant concentration is much higher than that of the V(IV) product the error is rather small. This error has been discussed.[8]

[10] The rate of the $V(H_2O)_6^{3+}$–H_2O solvent exchange can be estimated from the anation rate with thiocyanate (B. R. Baker, N. Sutin, and T. Welch, *Inorg. Chem.*, **6**, 1948 (1967)) and azide ions (J. H. Espenson and J. R. Pladziewicz, 159th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969).

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

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

280 M^{-1} sec^{-1} at 0.80 M H$^+$, 25.0°, μ = 2.0 M), if V(V) is formed in the V(III)-Cr(VI) it should accumulate at easily detected levels. Moreover, the rate of formation of V(IV) would be lower than the rate of loss of V(III). Both of these points should be subject to direct experimental testing, and it should thereby be possible to make a firm distinction between a one- and two-electron mechanism.

Experimental Section

Materials. Stock solutions of oxovanadium(IV) perchlorate were prepared by electrolytic reduction of vanadium pentoxide.[13] Vanadium(II) solutions were prepared by reduction with amalgamated zinc. Nearly stoichiometric amounts of V(II) and V(IV), with a slight excess (~2%) of the latter, were reacted to prepare V(III) stock solutions. The V(III) solutions were analyzed by reaction with $Co(NH_3)_5Br^{2+}$ using Cu^{2+} as catalyst.[4] A fresh solution of $Co(NH_3)_5Br^{2+}$ in perchloric acid (0.001 M) and copper(II) perchlorate (0.01 M) was prepared, and identical volumes were placed in each of several volumetric flasks. After flushing the solutions with purified nitrogen for at least 20 min the desired quantity of the V(III) solution was added to some of the flasks using a 1-ml syringe and a small-gauge 30-cm Teflon needle. The reaction was allowed to continue 20 min after which all the flasks were diluted to volume with water. The absorbances of the reaction solutions and of the solutions to which V(III) had not been added were measured at λ 253 nm, an absorption maximum for $Co(NH_3)_5Br^{2+}$ (ϵ 1.67 × 10^4 M^{-1} cm^{-1}). The decrease in the $Co(NH_3)_5Br^{2+}$ concentration, computed from the absorbance difference, was taken as the V(III) concentration based on the known 1:1 stoichiometry. The results were generally within 5% of the known total vanadium in the solution, the remainder being V(IV).

Potassium dichromate was recrystallized three times, and lithium perchlorate, prepared from the carbonate, twice. Conductivity water was used throughout.

Procedures. Many of the rate constant determinations were made using a Durrum stopped-flow instrument with a Kel-F mixing chamber and a 2-cm optical path. Other determinations were made using the Atom Mech apparatus described previously.[14,15] The values obtained using the two different instruments agreed to within experimental error. Pseudo-first-order rate constants were calculated from the slopes of the usual plots, and second-order constants by division of the average V^{3+} concentration in the run.

The yields of I_2 produced in the induced oxidation of iodine were determined spectrophotometrically at λ 465 nm, having calibrated the apparent molar absorptivity of I_2 as a function of I^- concentration. The oxidation of V^{3+} by I_2 occurs rather slowly, but it is not negligible. Even when the induced oxidation studies were carried out directly in the spectrophotometer cell to be used for analysis, a small extrapolation was needed to correct for this secondary reaction. The absorbances from which the I_2 yields were calculated were corrected for the small contribution of V(III) at λ 465 nm as well.

Reaction Conditions. In all experiments lithium perchlorate was used to maintain 1.00 M ionic strength. The absorbance changes were monitored at several wavelengths depending upon the concentrations of the species present and upon the purpose of that set of experiments. Most of the rate constant evaluations were made at λ 350 nm, where $HCrO_4^-$ has an absorption maximum (ϵ 1560 M^{-1} cm^{-1}); a few studies of the same rate were carried out by following the increasing absorption of VO^{2+} at λ 760 nm (ϵ 17.0). Studies to detect the possible presence of VO_2^+ were carried out in the uv where its absorption is quite substantial: λ 313 nm, $HCrO_4^-$ (711), VO_2^+ (400); λ 280 nm, $HCrO_4^-$ (1530), VO_2^+ (725); and λ 226 nm, $HCrO_4^-$ (1725), VO_2^+ (1736). At the low Cr(VI) concentrations employed, the dimeric form $Cr_2O_7^{2-}$ is negligible in concentration,[16] although not necessarily negligible in reactivity.[4a,7b] Other equilibria of importance are the protonation of $HCrO_4^-$,[16] and the acid dissociation of $V(H_2O)_6^{3+}$.[17] The incorporation of these reactions will be considered in a subsequent section.

Results

Stoichiometry. The coefficients in reaction I were verified by analyzing for the concentration of V(III) remaining after reaction with an insufficient quantity of $HCrO_4^-$. In two experiments at 0.200 M H$^+$ the following results were obtained

$10^4[HCrO_4^-]_0$	$10^4[V^{3+}]_0$	$10^4[V^{3+}]_\infty$	R
1.03	5.07	1.99	2.99
0.62	5.07	3.24	2.96

where R = moles of V^{3+}/mole of Cr^{VI} reacted.

In the presence of excess Cr(VI) oxidation to V(V) is expected, as shown in reaction II. Although rate stud-

$$3V^{3+} + 2HCrO_4^- + 2H^+ = 3VO_2^+ + 2Cr^{3+} + 2H_2O \quad \text{(II)}$$

ies were not carried out with excess Cr(VI), the stoichiometry under such conditions was considered. After reaction the excess Cr(VI) was analyzed by the method of Rowland.[18] The results are as follows.

$10^4[V^{3+}]_0$	$10^4[HCrO_4^-]_0$	$10^4[HCrO_4^-]_\infty$	R
0.617	2.00	0.157	1.44
0.617	2.00	0.159	1.50
0.937	2.00	0.142	1.62
0.937	2.00	0.142	1.62

Both of these determinations substantiate that reaction I occurs as written, and that Cr(VI) functions as a three-equivalent oxidizing agent.

Rate Studies at Low [H$^+$]. In the range 0.005 ≤ [H$^+$] ≤ 0.04 M the protonation equilibrium of $HCrO_4^-$ referred to earlier is negligible.[16] In this range of [H$^+$], rate studies were carried out over an 18-fold variation of [V^{3+}] and a 20-fold variation of [$HCrO_4^-$]. Small corrections were made for the acid dissociation of V^{3+} using K_a = 0.0014 M,[17] and second-order rate constants were calculated according to the expression given in eq 1. The individual rate experiments are cited in

$$-d[HCrO_4^-]/dt = k[V^{3+}][HCrO_4^-] \quad (1)$$

Table I. The average value of k is 386 ± 14 M^{-1}

Table I. Second-Order Rate Constants for the Reaction of V^{3+} with $HCrO_4^-$ at Low [H$^+$][a]

Initial concn, M			k, M^{-1} sec^{-1} [b]
[H$^+$]	$10^4[HCrO_4^-]$	$10^4[V^{3+}]$	
0.00500	0.20	10.8	405
0.0100	1.00	13.1	406
0.0100	0.200	20.0	399
0.0100	0.100	41.0	410
0.0100	0.200	10.9	388
0.0200	1.00	12.0	436
0.0200	1.00	23.7	433
0.0200	1.00	23.8	437
0.0200	0.500	25.6	406
0.0200	1.00	52.0	377
0.0200	0.200	52.7	387
0.0200	1.00	53.0	360
0.0200	2.00	36.3	399
0.0200	0.200	97.1	373
0.0200	1.00	10.4	366
0.0200	1.00	19.4	381
0.0400	1.00	23.9	369

[a] Evaluated at λ 350 nm at μ = 1.00 M and 25.0°. [b] Corrected for the acid dissociation of V^{3+} by multiplication of the calculated second-order rate constant by the factor (K_a + [H$^+$])/[H$^+$] with K_a = 0.0014 M.

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(13) J. H. Espenson and R. J. Christensen, *J. Amer. Chem. Soc.*, **91**, 7311 (1969).

(14) O. J. Parker and J. H. Espenson, *ibid.*, **91**, 1313 (1969).

(15) (a) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963); (b) D. W. Carlyle and J. H. Espenson, *ibid.*, **6**, 1370 (1967).

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

(17) L. Pajdowski, *J. Inorg. Nucl. Chem.*, **2**, 433 (1966).

(18) G. P. Rowland, Jr., *Ind. Eng. Chem., Anal. Ed.*, **11**, 442 (1939).

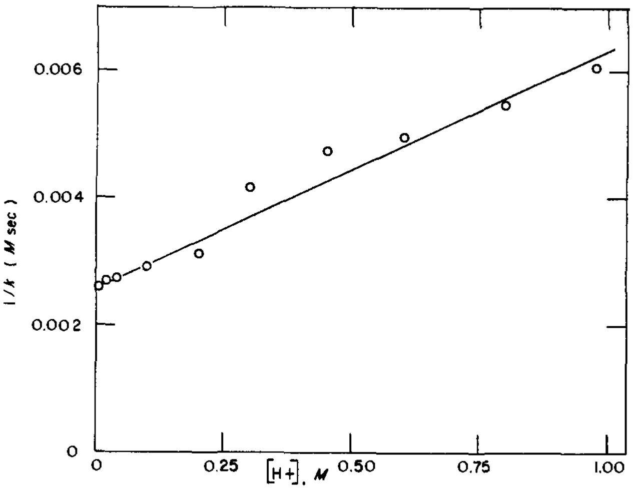

Figure 1. A plot of the reciprocal of the apparent second-order rate constant *vs.* $[H^+]$.

sec^{-1}. No dependence of k on $[HCrO_4^-]$ was noted, indicating $Cr_2O_7^{2-}$ has a much lower reactivity than $HCrO_4^-$ does under these conditions. A slight trend was noted in the value of k with V^{3+} concentration, barely outside the experimental error; this deviation can be attributed to a small contribution at low $[V^{3+}]$ from the reaction[7] of VO^{2+} (a product) and $HCrO_4^-$ which is considered in an accompanying paper.[8]

Rate Studies at $[H^+] \geq 0.1$ *M*. Additional rate measurements were carried out at higher acid concentration, $0.10 \leq [H^+] \leq 0.96$ *M*, again with V^{3+} in considerable excess over $HCrO_4^-$, usually by >50-fold. The results are summarized in Table II. Under the conditions the equilibrium shown in reaction III is important. Various determinations of K_{Cr} are re-

$$H_2CrO_4 = H^+ + HCrO_4^- \qquad K_{Cr} \qquad \text{(III)}$$

ported, with values[16,19] in the range 1-5 *M*. Assuming that the only significant rate term was that given by eq 1 (*i.e.*, that H_2CrO_4 is an unreactive form), the true value of k for the species $HCrO_4^-$ is related to the apparent (experimental) value by the expression given in eq 2. The value of k_{app} is based on the total Cr(VI) concentration. A test of this relation can be made in a plot of

$$k = k_{app}(1 + [H^+]/K_{Cr}) \qquad (2)$$

$1/k_{app}$ *vs.* $[H^+]$, which should be a straight line having $1/k$ as intercept and $1/kK_{Cr}$ as slope. The plot, given in Figure 1, leads to the values $k = 390\ M^{-1}\ sec^{-1}$ and $K_{Cr} = 0.69\ M$. The calculated and experimental values of k_{app} differ by an average of 5.1%. The value of K_{Cr} derived from this treatment lies outside the range of most of the reported determinations,[15,18] but the literature values are subject to considerable uncertainty, primarily because H_2CrO_4 is such a strong acid. For instance, under one set of assumptions concerning the species present, Tong and King[16] calculate $K_{Cr} = 1.2$ *M*, whereas under the assumption $HCr_2O_7^-$ does not attain appreciable concentration, Tong[19d] derives the value 4 *M* from the same original experimental data. One might have proceeded in the present case by selecting a particular value of K_{Cr} but at least two further parameters would then be needed to describe the dependence upon $[H^+]$. The most realistic approach appears to be to indicate that the data obtained are in accord with eq 2, and that the value of K_{Cr} so derived, while low, is not unreasonable.

Table II. Second-Order Rate Constants for the Reaction of V^{3+} with $HCrO_4^-$ at High $[H^+]$[a]

—Initial concn,[b] *M*—		k_{app},[c] $M^{-1}\ sec^{-1}$	
$[H^+]$	$10^4[V^{3+}]$	Obsd	Calcd[d]
0.100	53.0	345	337
0.200	48.1	318	299
0.300	54.0	239	269
0.450	52.0	212	234
0.600	26.2	195	206
0.600	54.0	196	206
0.600	10.0	212	206
0.600	2.06	203	206
0.800	49.3	183	179
0.960	54.0	165	161

[a] Evaluated at λ 350 nm at $\mu = 1.00$ *M* and 25.0°. [b] The initial $HCrO_4^-$ concentration is 1.00×10^{-4} *M* in all these runs. [c] Defined by the relation $-[V^{3+}]_{av}^{-1}$ (d ln [Cr(VI)]/d*t*); the values given are the average of three to four determinations with a given set of solutions. [d] According to eq 2 using the values of k and K_{Cr} given in the text.

Other Rate Studies. Attempts were made to distinguish whether the initial oxidation of V(III) by Cr(VI) occurs in a one- or two-equivalent step. Rate studies are not necessarily effective, however, since if the reactions subsequent to the first occur rapidly, they exert no net effect upon either the stoichiometry of the kinetics. If a two-equivalent reaction is effective, the pair of products Cr(IV) + V(V) is formed. Among the subsequent reactions needed, should that be the case, is the reaction of V(III) and V(V). With high $[H^+]$ the apparent second-order rate constants for the oxidation of V(III) by $HCrO_4^-$ and by VO_2^+ are of the same order of magnitude; for instance, the values are 180 and 280 $M^{-1}\ sec^{-1}$, respectively, at 0.80 *M* H^+.

Three types of experiments suggest themselves: (1) in the uv the molar absorptivity of VO_2^+ is quite large, so evidence for its possible primary formation can be sought directly; (2) rate studies can be carried out in the uv where $HCrO_4^-$ and VO_2^+ absorb appreciably—a two-equivalent mechanism in which VO_2^+ partially accumulates will probably show deviations from simple pseudo-first-order kinetics, or at least the rate constant will have a different value; (3) the reaction can also be studied at λ 760 nm where VO^{2+} is the only species with substantial absorption, to study whether it is produced at the same rate as V(III) is oxidized (as in the one-equivalent mechanism), or whether is produced at a different rate as the product of a secondary reaction. The experimental results are as follows.

At both λ 226 and 280 nm the absorbance change corresponded to a simple one-step pseudo-first-order decrease as would be the case if only $HCrO_4^-$ and not VO_2^+ as well was providing the main absorbance contribution. The rate constants at these wavelengths as well as at λ 760 nm were within experimental error of

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(19) (a) N. Bailey, A. Carrington, K. A. Lott, and M. C. R. Symons, *J. Chem. Soc.*, 290 (1960); (b) G. P. Haight, D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, 3, 1777 (1964); (c) D. G. Lee and R. Stewart, *J. Amer. Chem. Soc.*, **86**, 3051 (1964); (d) J. Y. Tong, *Inorg. Chem.*, 3, 1804 (1964); (e) M. Orhanović and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 278 (1967).

the values (cited above) evaluated at λ 350 nm.[20] The results are as follows.

λ, nm	$10^4[HCrO_4^-]$	$10^4[V^{3+}]$	k, M^{-1} sec^{-1}
226	0.20	58.0	175
280	0.30	100	183
760	0.30	103	174

A number of other experiments were made at λ 760 nm with rate constants lower by 10–15% but showing no apparent deviation from pseudo-first-order kinetics. This probably results from interference of the VO^{2+}–$HCrO_4^-$ reaction, and it appears that under all the conditions studied here the one-equivalent sequence in which V(V) is not involved provides the dominant mechanism.

Induced Oxidation of Iodide Ion. In accord with the findings of Luther and Rutter,[3] it was found here that the V(III)–Cr(VI) reaction does induce the oxidation of I^-. Production of iodine occurs at a rate much higher than it does from the oxidation of I^- by Cr(VI) under the same conditions. The induction factor, F_i, defined as the ratio of the moles of I^- oxidized to the moles of V(III) oxidized, was determined as follows. Solutions having known $[I^-]/[V^{3+}]$ ratios were treated with a small but known concentration of $HCrO_4^-$, *ca.* 10^{-4} M. The iodine concentration ($I_2 + I_3^-$) was determined spectrophotometrically after a small correction for the slow V^{3+}–I_3^- reaction as described above. The iodine yield gave the number of moles of I^- oxidized. The V(IV) yield was then taken as that part of the total oxidizing power of the Cr(VI) added not expended toward the oxidation of iodide ions.

The values of F_i were measured as a function of the $[I^-]/[V^{3+}]$ ratio, and as a function of acid concentration in the range $0.005 \leq [H^+] \leq 0.04$ M. The dependence of F_i on the reactant ratios is illustrated by the results at 0.02 M H^+, summarized in Table III. The values clearly approach the limit $F_i = 2.0$. The hydrogen ion concentration does affect the reactant ratio at which the limit is reached. Figure 2 depicts the approach to the limiting F_i value as a function of $[I^-]/[V^{3+}]$ at various $[H^+]$ from which it is easily seen that a lower $[H^+]$ demands a higher value of the ratio $[I^-]/[V^{3+}]$ to attain the limit.

Table III. Induced Oxidation of Iodide Ion at 0.020 M H^+, 25°, $\mu = 1.0$ M

$10^3[V(III)]_0$, F	$[I^-]/[V^{3+}]_0$[a]	F_i[b]
4.88	0.25	0.152
2.12	0.303	0.284
1.95	0.50	0.212
1.95	0.62	0.403
0.98	1.00	0.603
0.99	1.02	0.69
0.98	1.23	0.73
0.99	1.96	1.02
0.98	2.38	1.26
0.97	2.41	1.26
0.99	3.26	1.41
0.98	4.76	1.46
0.97	4.82	1.65
0.99	6.52	1.75
0.99	7.38	1.75
0.98	9.52	1.94
0.51	11.9	1.97
0.99	13.1	1.90
0.99	15.1	1.94

[a] $[V^{3+}]_0$ derived from $[V(III)]_0$ using $K_a = 0.0014$ M. [b] Moles of I^- oxidized/mole of V(III) oxidized.

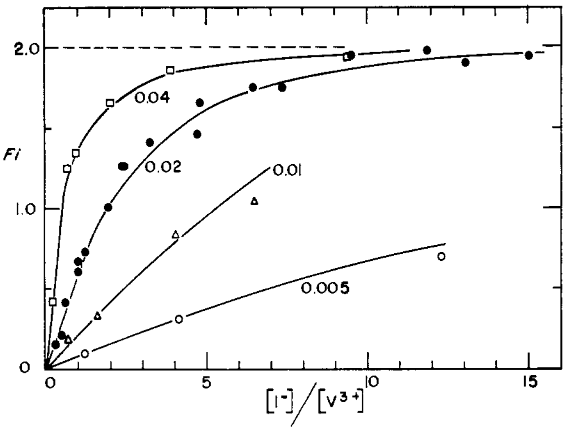

Figure 2. The approach to a limiting value of the induction factor F_i as a function of the $[I^-]/[V^{3+}]$ ratio at different hydrogen ion concentrations.

Interpretation and Discussion

The Oxidation of V^{3+}. The reaction kinetics as described by eq 1 and 2 are consistent with a single transition state formed according to the following net activation process.[21]

$$V^{3+} + HCrO_4^- = [VHCrO_4^{2+}]^{\ddagger} \xrightarrow{H_2O} VO^{2+} + H_3CrO_4 \quad \text{(IV)}$$

That a different dependence upon $[H^+]$ was not noted is not surprising because the formula H_3CrO_4 that thereby follows for chromium(V) is the same as that deduced from the study of the V(IV)–Cr(VI) reaction and from the Fe(II)–Cr(VI) reaction.

The first step of the Fe^{2+}–$HCrO_4^-$ process proceeds by a similar reaction, and indirect evidence,[4a] partly confirmed by experiment,[4b] suggested an inner-sphere mechanism. Can a similar detailed mechanism be proposed here? Direct evidence is lacking because the aquation of the product vanadium(IV) complex, were such a species formed, would be expected to occur rapidly.

Another approach to an answer to the same question is as follows: The anation of $V(H_2O)_6^{3+}$ generally takes place at a specific rate lower than that determined here for $V^{3+} + HCrO_4^-$; a typical anation rate constant[10] is 117 M^{-1} sec^{-1} for the reaction of V^{3+} with NCS^-. This comparison suggests that the reaction of V^{3+} and $HCrO_4^-$ probably occurs without prior complexation because it occurs more rapidly than water loss from the primary coordination sphere of V^{3+}. This conclusion we have reached is, however, only a tentative one because (a) the solvent exchange rate of $V(H_2O)_6^{3+}$ is not known directly but only by inference from the anation rates,[10] and (b) the conformity of

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[20] The 3:1 reaction stoichiometry does not enter in these considerations: the rate constant at λ 760 nm is still that defined by eq 1; a value three times as big does *not* result because V^{3+} is still in excess. Even though VO^{2+} makes the only significant absorbance contribution, the slope of the pseudo-first-order absorbance plot is $-d \ln [HCrO_4^-]/dt$ and not $-3d \ln [HCrO_4^-]/dt$.

[21] T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, 63, 365 (1959).

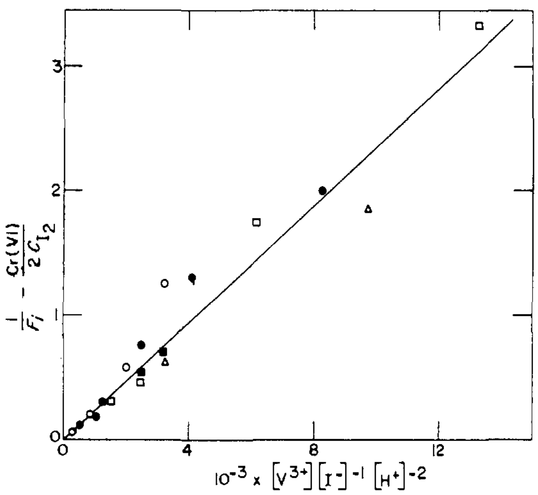

Figure 3. Correlation of the induced oxidation of iodide as a function of the concentration variables in a plot according to eq 5. Different $[H^+]$'s are represented as follows: 0.0050 *M*, triangles; 0.0058 *M*, filled squares; 0.0100 *M*, open squares; 0.0200 *M*, closed circles; and 0.0400 *M*, open circles.

V^{3+} to the general pattern[22] of octahedral substitution, in which anation rates are limited by the rate of dissociation of coordinated water, has not been established (and, in fact, appears a rather questionable matter).[10]

Reaction IV produces VO^{2+} and Cr(V) rather than V(V) and Cr(IV) for reasons cited above. For the same reasons the unimportance of V(V) in the subsequent rapid mechanistic steps, about which no direct information is obtained from the kinetics, is also established. Consequently, the reaction following step IV produces V(IV) + Cr(IV) and not V(V) + Cr(III). The last step, also rapid, needed to conform to the stoichiometry and rate results is that shown in Scheme I. Aside from establishing the oxidation state changes occurring in the successive stages, the kinetic data, in themselves, do not yield information concerning the rate or rate dependences contained in the rapid steps.

The Rate Expression for the V(III)–Cr(V) Reaction. The study of the induced oxidation of iodide established[2] the important role of Cr(V) as an intermediate corresponding to the limiting induction factor of 2.0. The reaction of Cr(V) occurring in the absence of I^- is shown in Scheme I; in the presence of iodide ion an alternate reaction becomes available, represented by the following steps (reaction V is known[4b,7b,8] to be first order in $[H^+]$).

$$H_3CrO_4 + I^- + H^+ \longrightarrow Cr^{III} + HOI \qquad (V)$$

$$I^- + HOI + H^+ = I_2 + H_2O \qquad (VI)$$

The quantitative interpretation of the variation of F_i with the $[I^-]/[V^{3+}]$ ratio is given according to the following development.[7b]

The initial step, reaction IV, occurs as written irrespective of I^- and V^{3+} concentrations so that the minimum concentration of VO^{2+} produced is $[HCrO_4^-]_0$. Representing the concentration of V(IV) produced by the subsequent steps as *x* and the concentration of iodide ion consumed by Cr(V) as *y*, the competition for Cr(V) is given by the rate ratios of the competing reactions

$$\frac{dx}{dy} = \frac{k_{35}[V^{3+}][H^+]^n}{k_V[I^-][H^+]} \qquad (3)$$

where k_{35} is the rate constant for the reaction of V(III) and Cr(V) which exhibits an *n*th order dependence on $[H^+]$. Since the concentration of Cr(VI) was small relative to $[V^{3+}]$ and $[I^-]$, the latter values remain nearly constant; *x* and *y* thus increase at a constant ratio during the run. Consequently, x_{eq}/y_{eq} may replace d*x*/d*y*. The substitution $y_{eq} = 2C_{I_2}$ is made, where C_{I_2} represents the formal iodine(0) concentration, $[I_2] + [I_3^-]$. The expression for the induction factor is given by eq 4 and upon substitution of $2C_{I_2}$

$$F_i = \frac{y_{eq}}{[Cr^{VI}]_0 + x_{eq}} \qquad (4)$$

for y_{eq}, and of x_{eq} from eq 3, the following expression is obtained after rearrangement.

$$\frac{1}{F_i} - \frac{[Cr^{VI}]_0}{2C_{I_2}} = \frac{k_{35}[V^{3+}][H^+]^n}{k_V[I^-][H^+]} \qquad (5)$$

The observed dependence of F_i upon $[H^+]$ can be accounted for by introduction of $[H^+]^2$ in the denominator of the right-hand term, *i.e.*, $n = -1$. A plot constructed according to eq 5 is presented in Figure 3, in which data covering the range $0.005 \leq [H^+] \leq 0.04$ *M* are included. The line is linear, justifying the assignment of $n = -1$. From the slope of the line the value $k_{35}/k_V = 2.8 \times 10^{-4}\ M^2$ was obtained. Consequently, it is inferred that the reaction of V(III) and Cr(V) occurs with a rate dependence on $1/[H^+]$. The net activation process[19] can be represented as

$$V^{3+} + H_3CrO_4 \longrightarrow [VH_2CrO_4^{2+}]^{\ddagger} + H^+ \qquad (VII)$$

This competition study allows us to ascertain the composition of the activated complex for the V(III)–Cr(V) reaction, an item not obtainable from the V(III)–Cr(VI) kinetic study because the Cr(V)–V(III) step occurs too rapidly. The study does not yield an absolute rate constant for reaction VII, only a value relative to that for the Cr(V)–I^- reaction. One cannot distinguish whether the reaction occurs between VOH^{2+} and H_3CrO_4 or between V^{3+} and $H_2CrO_4^-$. The first of these may be more likely, because other Cr(V) reactions do not show inverse $[H^+]$ dependences whereas VOH^{2+} is known to be a species often more reactive than V^{3+}.

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[22] (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967; (b) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966; (c) N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966); (d) J. H. Espenson and D. F. Dustin, *Inorg. Chem.*, 8, 1760 (1969), and references therein.