(based on the stoichiometry of eq 1) depends on reaction conditions. It is clear that the yield of the stable chromium(V) species is determined almost entirely by the excess of HMBA and is very approximately proportional to its concentration. It is essentially independent of the dominant kinetic term. As we have obtained no kinetic evidence for the formation of the HMBA–Cr(VI) complex in substantial concentrations, it seems most likely that chromium(V) is formed first as the free acid, H_3CrO_4, which subsequently reacts with HMBA to form a stable complex.

The stability of chromium(V) formed in the course of the chromic acid oxidation of 2-hydroxy-2-methylbutyric acid is much higher than that of any previously observed chromium(V) compound. There is little doubt that chromium(V) exists in the form of a complex with the hydroxy acid, and it is quite probable that the complex is cyclic. Ordinarily, one would expect that a cyclic complex between a two-electron oxidant and substrate which can easily react in a two-electron oxidation leading to carbon–carbon bond cleavage should be extremely unstable. In fact, a similar complex derived from chromium(VI) is held responsible for the very rapid chromic acid oxidation of ditertiary α-glycols.[29,30] Why the complex with a tertiary hydroxy acid should be so particularly stable is unclear. It is not clear whether this is due to a particularly low ability of chromium(V) to react by a cyclic reaction mechanism, or whether the principal factor is ligand stabilization of the chromium(V) species.

References and Notes

(1) Part 11: F. Hasan and J. Roček, *J Am. Chem. Soc.*, **98**, 6574 (1976).

(2) Support for this investigation by a grant of the National Science Foundation is gratefully acknowledged.

(3) F. Hasan and J. Roček, *J. Am. Chem. Soc.*, **97**, 1444 (1975).

(4) K. Chatterjee and B. P. Gyani, *J. Indian Chem. Soc.*, **36**, 605 (1959).

(5) T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, 1192, 3193 (1964).

(6) K. K. Sen Gupta, A. K. Chatterjee, and S. P. Moulik, *Bull. Chem. Soc. Jpn.*, **43**, 3841 (1970).

(7) K. K. Sen Gupta, A. K. Chatterjee, and J. K. Chakladar, *Indian J. Chem.*, **10**, 493 (1972).

(8) M. Krumpolc and J. Roček, *J. Am. Chem. Soc.*, **98**, 872 (1976).

(9) I. M. Kolthoff and R. Belcher in "Volumetric Analysis", Vol. III, Interscience, New York, N.Y., 1965, p 332.

(10) D. G. Holah and J. P. Fackler, Jr., *Inorg. Synth.* **10**, 26 (1967).

(11) "Handbook of Chemistry and Physics", 55th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1974.

(12) V. Srinivasan and J. Roček, *J. Am. Chem. Soc.*, **96**, 127 (1974).

(13) M. Krumpolc and J. Roček, to be submitted for publication.

(14) G. Charlot in "Colorimetric Determination of Elements", Elsevier, New York, N.Y., 1964, p 268.

(15) K. B. Wiberg and S. K. Mukherjee, *J. Am. Chem. Soc.*, **93**, 2543 (1971).

(16) "The Practice of Gas Chromatography", L. S. Ettre and A. Zlatkis, Ed., Interscience, New York, N.Y., 1967, p 390.

(17) W. W. Umbreit, R. H. Burris, and J. F. Stauffer in "Manometric Techniques", 4th ed, Burgess Publishing Co., Minneapolis, Minn., 1964, Chapter IV.

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

(19) "Comprehensive Chemical Kinetics", Vol. 7, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1972, p 510.

(20) (a) H. Kon, *Bull. Chem. Soc. Jpn.*, **35**, 2054 (1962); (b) *J. Inorg. Nucl. Chem.*, **25**, 933 (1963); (c) K. B. Wiberg and H. Schafer, *J. Am. Chem. Soc.*, **91**, 933 (1969).

(21) Cf. ref 3 and other preceding papers in this series.

(22) The value of K_a for 80 °C was calculated from the van't Hoff equation using the value[23] of $\Delta H^\circ = -207.9$ kcal mol^{-1} and the value[24] of K_a(25 °C) = 4.2 M.

(23) K. B. Wiberg in "Oxidation in Organic Chemistry", Part A, K. B. Wiberg, Ed., Academic Press, New York, N.Y., 1965, p 71.

(24) J. Y. Tong, *Inorg. Chem.*, **3**, 1804 (1964).

(25) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(26) As 2-hydroxy-2-methylbutyric acid is a weak acid ($K_a = 1.35 \pm 0.10 \times 10^{-4}$ M at 0.01 M and 25 °C, determined by potentiometric titration[27]), its dissociation under given experimental conditions can be neglected, and the undissociated form of the acid is practically equal to the total analytical concentration.

(27) A. Albert and E. P. Serjeant in "The Determination of Ionization Constants", Chapman and Hall, London, 1971, Chapter II.

(28) F. Hasan and J. Roček, *J. Am. Chem. Soc.*, **94**, 9073 (1972).

(29) A. K. Chatterjee and S. K. Mukherjee, *Z. Phys. Chem. (Leipzig)*, **208**, 281 (1958).

(30) Y. W. Chang and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 1401 (1960).

Chromic Acid Oxidation of Iodide[1]

George F. Vandegrift and Jan Roček*

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. Received July 28, 1976

Abstract: The chromic acid oxidation of iodide follows the rate law given in eq 26 of the text over a range of iodide concentrations from 4×10^{-4} to 2.0 M and of hydrogen ion (nitric acid) concentration from 0.3 to 1.0 M. The proposed mechanism postulates four reaction paths involving $ICrO_3H$, $ICrO_3H_2^+$, $I_2CrO_3H^-$, and I_2CrO_2 as reactive intermediates. Kinetic evidence has been obtained for the reaction $HCrO_4^- + I^- + H^+ \rightleftarrows ICrO_3^-$ with an equilibrium constant $K_1 = [ICrO_3^-]/([HCrO_3^-]\cdot[I^-]h_0) = 1.4 \pm 0.5$ at 25 °C and 2.0 M ionic strength ($NaNO_3$).

Of all the oxidation reactions routinely performed in chemical laboratories, few are used as commonly as the oxidation of iodide to iodine by chromic acid.

There have been several attempts to unravel the Cr(VI)–I^- redox reactions; none so far completely satisfactory. The earliest recorded work on the kinetics of this system was in 1903 by DeLury, who found that the reaction was first order in $Cr_2O_7^{2-}$, ca. second order in acid, and a mixture of first and second order in iodide ion.[2]

$$\text{Rate} = [Cr_2O_7^{2-}][H^+]^2(k_1[I^-] + k_2[I^-]^2) \qquad (1)$$

Beard and Taylor used chloride ion to keep constant ionic strength[3] and observed an interesting effect of chloride ion, which reduced the rate at low concentrations but accelerated it at concentrations higher than 0.7 M; for a solution 1.5 M in chloride they proposed the rate law:

$$\text{Rate} = 14.6[H^+][I] + 5.3 \times 10^4[H^+]^2[I^-]^2[Cr(VI)] \qquad (2)$$

Edwards[4] noted that their data fit equally well in the form:

$$\text{Rate} = k_1[CrI^-] + k_2[H^+][CrI^-] + k_3[I^-][CrI^-] + k_4[H^+][I^-][CrI^-] \qquad (3)$$

Howlett and Sarsfield[5] found a similar ionic strength effect with perchlorate with a minimum at 0.7 M. They also performed a study of the initial rate vs. dielectric constant of the solvent and obtained an excellent correlation of log(k) vs. $1/D$.

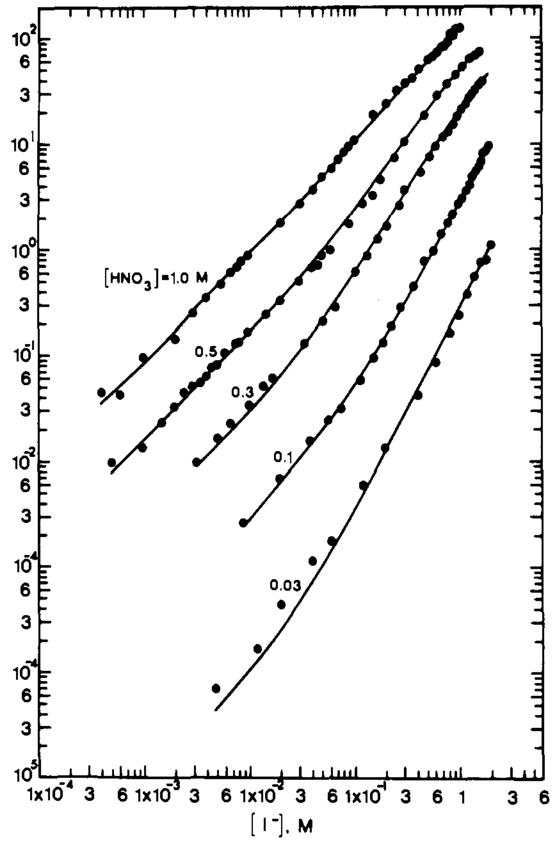

Figure 1. Dependence of experimental first-order rate constants, k_{exptl}, on iodide concentration at five nitric acid concentrations. Curves calculated from eq 10.

They arrive at the following rate laws for the full reaction (eq 4) and for its initial phase (eq 5), respectively.

$$\text{Rate} = \frac{6k_{11}K_{10}k_{12}[\text{Cr(VI)}]^2[\text{I}^-]^2}{k_{-11}[\text{I}_2] + k_{12}[\text{Cr(VI)}]} \qquad (4)$$

$$\text{Rate} = 6k_{11}K_{10}[\text{HCrO}_4^-][\text{H}^+]^2[\text{I}^-]^2 \qquad (5)$$

The most recent study was reported by Gaswick and Krueger.[6] They were unable to confirm the inhibition by I_2 reported above; their results fitted the rate law

$$-\text{d}[\text{HCrO}_4^-]/\text{d}t = [\text{HCrO}_4^-](k_1[\text{H}^+][\text{I}^-] + k_2[\text{H}^+]^2[\text{I}^-]^2 + k_3[\text{H}^+]^3[\text{I}^-]) \qquad (6)$$

The reported rate laws thus show considerable differences. Moreover, the reaction rates which we obtained for this reaction in connection with another study[7] could not be reconciled with any of the proposed rate laws. The reason for these discrepancies may be due to the quite narrow concentration ranges used in the earlier studies; the proposed rate laws may thus represent approximations valid only over that particular range of conditions. We therefore felt that a full reinvestigation of this important reaction was required.

Experimental Section

All chemicals used were of AR grade or better. KI was used as a source for iodide. Nitric acid was the hydrogen ion source and $NaNO_3$ was used to keep ionic strength constant at 2 M. Perchloric acid was used in one case (0.5 M [H^+]) and no change was determined in the shape of the absorption vs. time curves or in the calculated rate constants. Two procedures were used in the determination of reaction rates. Stopped flow techniques were employed for fast reactions with half-lives of 5 ms to 30 s.[7] Slower reactions with half-lives over 5 s were carried out in a thermostated cell compartment of a Cary 15 spectrophotometer. Good agreement between the rate constants obtained by the two methods in the overlap region (half-lives of 5-30 s) was obtained. All measurements were monitored at 353 nm at 25 °C.

In slower reactions, where air oxidation became an important competing reaction, special precautions to remove dissolved oxygen were employed. Stock solutions were degassed by three cycles of freezing, evacuation, and thawing; the solutions were then stored and handled in the oxygen free atmosphere of a dry box. Inside the dry box, 1 ml of a solution containing KI and $NaNO_3$ was put into a 1-cm quartz cell and 1 ml of a solution containing K_2CrO_4 and nitric acid was put into a syringe fitted with a long teflon needle. The reaction was initiated inside the Cary 15 cell compartment, which was flushed with a stream of prepurified N_2, by forcing the contents of the syringe into the cell. Both the solution in the cell and in the syringe were equilibrated to 25 °C. This set of operations achieved excellent results with no air oxidation noticeable over 20 half-lives of the chromic acid-iodide reaction.

The reactions all gave good first-order kinetics at high acid concentrations. When the nitric acid concentration was reduced to 0.03 M, however, a new phenomenon began to develop. In runs with iodide concentration of about 0.2 M and above the reactions gave good straight line first-order plots for as much as 4 half-lives. However, at concentrations at about 0.1 M, the $\log(A - A_\infty)$ in time plots began to show an increase in slope with time; this phenomenon reported already by Gaswick and Krueger[6] becomes particularly noticeable at very low iodide concentrations. Initial rates were used under these conditions.

Results

Figure 1 shows a dependence of the observed pseudo-first-order rate constant on the initial concentration of iodide ions over a concentration range of about 10^4 at several acidities (0.03-1 M) at constant ionic strengths. At the two lowest acidities the slope of the log-log plot is approximately 2.0, corresponding to the second-order dependence for high iodide concentration consistent with the observations reported by previous investigators. At high acidity (1.0 M HNO_3) the slope is about precisely 1.0 throughout the whole range from 4×10^{-4} to 1.0 M. This behavior is in complete disagreement with rate laws 1-5. It could be reconciled with a rate law of the type represented by eq 6 only if the $k_2[\text{H}^+]^2[\text{I}^-]^2$ term became negligibly small compared with the $k_3[\text{H}^+]^3[\text{I}^-]$ term; however, this is inconsistent with the observed acidity dependence. The most interesting behavior is exhibited by measurements at intermediate acidities (0.3 and 0.5 M HNO_3); the S-shaped curves indicate an increase in order from first towards second order at intermediate iodide concentrations and a drop back to a first-order dependence at high iodide concentrations. This concentration dependence is completely inconsistent with any of the previously proposed rate laws.

A better insight is obtained if one inspects the plot of $k_{\text{exptl}}/[\text{I}^-]$ vs. [I^-] (Figure 2). At low acidities a straight-line dependence indicates that the reaction is essentially second order in iodide. The first-order term given by the intercept is very small for 0.03 M HNO_3, but much more significant at higher acidities.

At higher acidities the second-order rate constants first increase, but reach a constant value at high iodide concentrations; the higher the acidity the earlier the iodide-independent region is reached. It should be noted that at the highest acidities the range of values for the second-order rate constants is very small. In 1.0 M HNO_3 the value of the second-order rate constant, $k_{\text{exptl}}/[\text{I}^-]$, increases only by a factor of 2, although the iodide concentration is increased 5000 times; this is responsible both for the nearly first-order behavior observable in Figure 1 as well as for the considerable spread of experimental points in Figure 2.

The change from second to first order at the three high acidities is indicative of a mechanism involving the formation of a chromium-iodide intermediate (Scheme I), where the rate constants k_1 and k_2 have acid dependencies which must be

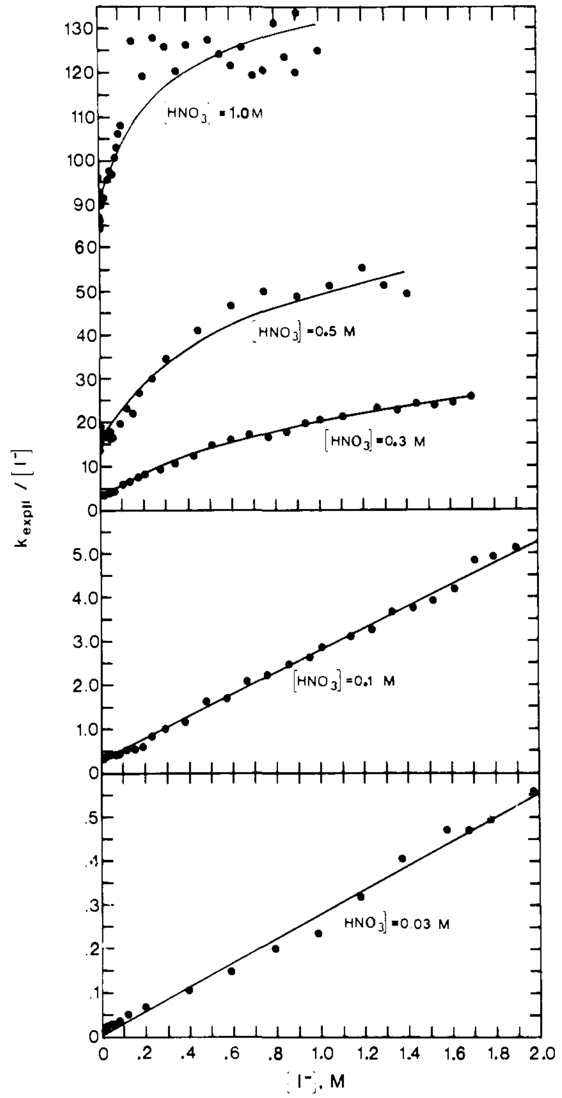

Figure 2. Dependence of $k_{\text{exptl}}/[I^-]$ on iodide concentration at five nitric acid concentrations. Curves calculated from eq 10.

determined through evaluating these parameters at various acid concentrations.[8]

Scheme I

$$HCrO_4^- + I^- + H^+ \overset{K_I}{\rightleftharpoons} ICrO_3^- \quad (7)$$

$$CrO_3I^- + \xrightarrow{k_1} \text{products} \quad (8)$$

$$CrO_3I^- + I^- \xrightarrow{k_2} \text{products} \quad (9)$$

The rate expression 10 derived from Scheme I and taking into account the dissociation of chromic acid, $H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$,

$$\frac{k_{\text{exptl}}}{[I^-]} = \frac{d([I_3^-]/[I^-])}{dt}$$

$$= \frac{K_I[H^+](k_1 + k_2[I^-])}{1 + K_I[H^+][I^-] + [H^+]/K_a^{H_2CrO_4}} \quad (10)^9$$

was used to fit the experimental data on an IBM 370 computer using a non-linear least-squares fitting subroutine, Harwell VAO2A.[10] In this way the best values of k_1, k_2, and K_I were obtained for 0.3, 0.5, and 1.0 M HNO_3 (Table I, k_1 and k_2 values in parentheses). The average value of

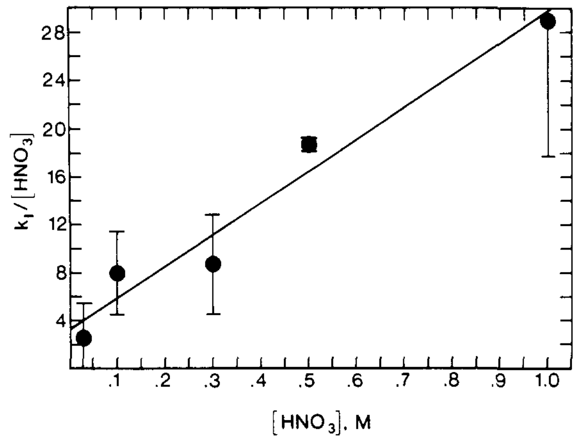

Figure 3. Dependence of k_1 on the concentration of nitric acid.

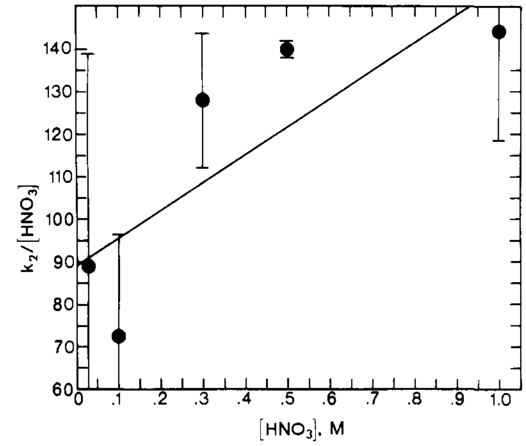

Figure 4. Dependence of k_2 on the concentration of nitric acid.

$$K_I = 3.4 \pm 1.1 \quad (11)$$

obtained from these three sets of measurements was then used to obtain the best values of k_1 and k_2 for each acidity. These values are listed in Table I and were also used to construct the calculated curves in Figures 1 and 2.

This value of K_I is based on the concentration of nitric acid ($K_I = [ICrO_3^-]/([HCrO_4^-][I^-][HNO_3])$); redefining it in terms of h_0[7] ($K_I = [ICrO_3^-]/([HCrO_4^-][I^-]h_0)$) gives a value of $K_I = 1.4 \pm 0.5$ M^{-2}. This value can be compared with the $K = 11.1$ M^{-2} for Cl[11] and $K = 3.3$ M^{-2} for Br.[12] The tendency to form halochromates, $XCrO_3^-$, thus decreases along the series Cl > Br > I.

The values of k_1 and k_2 show a definite dependency on acidity (Table I). The acidity-independent constants k_1', k_1'', k_2', and k_2'' were obtained by a weighted least-squares fit (Figures 3 and 4):

$$k_1 = k_1'[H^+] + k_1''[H^+]^2$$
$$k_1' = 3.2 \pm 1.6 \quad (12)$$
$$k_1'' = 26 \pm 3$$

and

$$k_2 = k_2'[H^+] + k_2''[H^+]^2$$
$$k_2' = 89 \pm 14 \quad (13)$$
$$k_2'' = 68 \pm 27$$

The values of K_I in Table I also show an acidity dependence, which would suggest the formation of $ICrO_3H$ besides $ICrO_3^-$. However, substantial protonation of $ICrO_3^-$ in solution of 0.5

Table I. Rate and Equilibrium Constants Obtained by Computer Fitting of Experimental Rates to Equation 10

$[HNO_3]$, M	k_1, s^{-1} M^{-1}	$k_1/[HNO_3]$, s^{-1} M^{-2}	k_2, s^{-1} M^{-2}	$k_2/[HNO_3]$, s^{-1} M^{-3}	K_1, M^{-2}
0.03	0.077 ± 0.087	2.6 ± 2.9	2.7 ± 1.5	89. ± 50	
0.1	0.80 ± 0.35	8.0 ± 3.5	7.2 ± 2.4	72. ± 24.	
0.3	2.60 ± 0.09 (3.78 ± 0.96)	8.7 ± 4.2	38.4 ± 0.2 (42.9 ± 1.6)	128. ± 16.	2.7 ± 0.5
0.5	9.33 ± 0.10 (9.20 ± 0.67)	18.7 ± 0.5	70.2 ± 0.5 (69.9 ± 1.0)	140. ± 2.	3.5 ± 0.2
1.0	28.9 ± 0.1 (17.8 ± 6.2)	28.9 ± 11.2	144.4 ± 0.3 (100 ± 0.9)	144. ± 31.	5.9 ± 2.1

and 1.0 M HNO_3 appears quite unlikely. Further, the standard deviations in the values of K_1 are too large to permit any more definite conclusions about its acidity dependence.

The rate constants k_1', k_1'', k_2', and k_2'' correspond to the following reactions:

$$ICrO_3^- + H^+ \xrightarrow{k_1'} \text{products} \quad (14)$$

$$ICrO_3^- + 2H^+ \xrightarrow{k_1''} \text{products} \quad (15)$$

$$ICrO_3^- + H^+ + I^- \xrightarrow{k_2'} \text{products} \quad (16)$$

$$ICrO_3^- + 2H^+ + I^- \xrightarrow{k_2''} \text{products} \quad (17)$$

Mechanism. A mechanism consistent with the kinetic results is given in Scheme II, where $K_{18}k_{19} = k_1'$, $K_{18}K_{20}k_{21} = k_1''$, $K_{22}k_{23} = k_2'$, and $K_{22}K_{24}k_{25} = k_2''$.

The rate law derived from this mechanism is given in eq 26. The mechanism suggests that the oxidation occurs through intermediate complexes containing chromium(VI) and one or two iodine atoms. The 1:1 complex can react either in its neutral form, $ICrO_3H$, or in the protontated form, $ICrO_3H_2^+$. It should be noted that within the acidity range used in this study (0.03-1.0 M HNO_3, corresponding to h_0 = 0.072-2.4) we did not observe any evidence of a first-order term in hydrogen ions which would correspond to the reaction

Scheme II

$$HCrO_4^- + I^- + H^+ \overset{K_1}{\rightleftarrows} ICrO_3^- \quad (7)$$

$$ICrO_3^- + H^+ \rightleftarrows ICrO_3H \quad (18)$$

$$ICrO_3H \rightarrow \text{products} \quad (19)$$

$$ICrO_3H + H^+ \rightleftarrows ICrO_3H_2^+ \quad (20)$$

$$ICrO_3H_2^+ \rightarrow \text{products} \quad (21)$$

$$ICrO_3^- + I^- + H^+ \rightleftarrows I_2CrO_3H^- \quad (22)$$

$$I_2CrO_3H^- \rightarrow \text{products} \quad (23)$$

$$I_2CrO_3H^- + H^+ \rightleftarrows I_2CrO_2 \quad (24)$$

$$I_2CrO_2 \rightarrow \text{products} \quad (25)$$

$$\text{Rate} = \frac{K_1[HCrO_4^-][I^-][H^+]^2(k_1' + k_1''[H^+] + k_2'[I^-] + k_2''[I^-][H^+])}{1 + K_1[I^-][H^+] + [H^+]/K_a^{H_2CrO_4}} = k_{\text{exptl}}[HCrO_4^-] \quad (26)$$

$$ICrO_3^- \rightarrow \text{products} \quad (27)$$

although such a term was present in several of the earlier published rate laws. It is feasible this term does become observable at lower acidities; this is suggested by the positive deviation of the experimental points from the calculated time for 0.03 M nitric acid at low iodide concentrations (Figure 2).

The 2:1 complex appears to react either in an anionic form, $I_2CrO_3H^-$, or as a neutral species, I_2CrO_2. However, due to the large uncertainty in the determination of k_2, existence of these two paths of decomposition for the 2:1 complex must be regarded with some reservation.

Whether the four reactions in which chromium(VI) is reduced (19, 21, 23, and 25) represent one- or two-electron oxidations cannot be determined from the available data.

References and Notes

(1) Support by the National Science Foundation is gratefully acknowledged.
(2) R. E. DeLury, *J. Phys. Chem.* 7, 239 (1903).
(3) R. F. Beard and N. W. Taylor, *J. Am. Chem. Soc.*, **51**, 1973 (1929).
(4) J. O. Edwards, *Chem. Rev.*, **50**, 455 (1952).
(5) K. E. Howlett and S. Sarsfield, *J. Chem. Soc. A*, 683 (1968).
(6) D. C. Gaswick and J. H. Krueger, *J. Am. Chem. Soc.*, **91**, 2240 (1969).
(7) G. F. Vandegrift and J. Roček, *J. Am. Chem. Soc.*, **98**, 1371 (1976).
(8) $[H^+] = [HNO_3]$; we found that at 2 M ionic strength ($NaNO_3$), h_0 is a linear function of the concentration of nitric acid, $h_0 = 2.4[HNO_3]$. However, because of the uncertainty in h_0 introduced at high iodide concentrations, we preferred to use the unambiguously defined $[HNO_3]$ rather than h_0.
(9) $K_a^{H_2CrO_4} = 10.0$ was used for all calculations. This value was extrapolated from data obtained at 20 °C by O. Lukkari, *Suom. Kemistil. B*, **43**, 347 (1970).
(10) For 0.03 and 0.1 M HNO_3 the denominator of eq 10 is very close to 1.0; consequently, a simple linear least-squares fit could be used.
(11) J. Y. Tong and R. L. Johnson, *Inorg. Chem.*, **5**, 1902 (1966).
(12) A. R. Zembrodt, Ph.D. Thesis, Ohio University, 1970.