Kinetics and Mechanism of the Chromium(VI)–Iodide Reaction

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Abstract: The kinetics of the chromium(VI)–iodide reaction have been measured spectrophotometrically in acidic, aqueous solution at 20.34° and 0.130 M ionic strength. The rate law obtained is $-d[HCrO_4^-]/dt$ (M sec^{-1}) = $[HCrO_4^-]\{0.206[H^+][I^-] + 111[H^+]^2[I^-]^2 + 154[H^+]^3[I^-]\}$. The rate is unaffected by the addition of Mn(II), Cl^-, or benzaldehyde. The mechanism of the reaction is presumed to involve the steps $Cr^{IV} + I^- \rightarrow Cr^{III} + I\cdot$ and $I\cdot + Cr^{VI} \rightarrow Cr^V + HOI$.

Mechanisms of Cr(VI) reduction have received intensive study involving both organic[2] and inorganic[3] reducing agents. An early review[4] established the classic Westheimer mechanism which, for two-electron reductants, may be expressed as

$$H_2A + Cr^{VI} \longrightarrow Cr^{IV} + A \quad \text{slow} \tag{1}$$

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

$$Cr^{V} + H_2A \longrightarrow Cr^{III} + A \tag{3}$$

The elucidation of steps subsequent to the rate-determining step has relied in part on the results of induced oxidations involving added species such as I^- or Mn(II). In fact, the presumed mechanism of the Cr(VI)–I^- reaction is derived from the behavior of systems in which induced oxidation of iodide occurs.[3a,b,4] The present study was undertaken to provide a direct examination of this important reaction

$$2HCrO_4^- + 9I^- + 14H^+ + 4H_2O \longrightarrow 2Cr(H_2O)_6^{3+} + 3I_3^- \tag{4}$$

and, in particular, to evaluate the appropriateness of steps 1–3 in describing this reaction.

An early study of the reaction was made by Beard and Taylor,[5] who reported the rate law

$$-d[HCrO_4^-]/dt = [HCrO_4^-]\{k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2\} \tag{5}$$

A very recent kinetic study[6] by the method of initial rates resulted in the rate law

$$-\frac{d[I^-]}{dt} = \frac{k_i k_{12}[Cr(VI)]^2[I^-]^2[H^+]^2}{k_{-11}[I_2] + k_{12}[Cr(VI)]} \tag{6}$$

In the present study it was felt desirable to work at low concentrations of Cr(VI) to minimize some of the complexities occurring in this system.[7] In addition an evaluation of the effects of added Mn(II) and Cl^- was desired.

Experimental Section

Reagents. Baker and Adamson (B&A) reagent grade K_2CrO_4 and KI were dried and used without further treatment. All other salts were of reagent quality and were used as received after drying. The kinetics were independent of the source of $HClO_4$, both Baker Analyzed 60% and B&A 72% being employed. Matheson Cl_2-free benzaldehyde was purified by vacuum distillation from KI crystals under nitrogen. Eastman White Label allyl acetate was used as received. Hexaaquochromium(III) perchlorate was prepared by the reduction of reagent CrO_3 with a slight excess of formic acid in 1 M $HClO_4$.[8] The solution was heated at 60° for 1 hr, concentrated on a rotary evacuator, and then recrystallized from 0.01 M $HClO_4$. The concentrations of the Cr(III) solutions were determined spectrophotometrically at 375 mμ[9] after alkaline oxidation with H_2O_2. Water was distilled from basic $KMnO_4$ and then redistilled.

Kinetics. The progress of the reaction was followed by measuring the absorbance of the solution at 353 mμ. At this wavelength, ϵ is 26,400 M^{-1} cm^{-1} for I_3^- and 1560 M^{-1} cm^{-1} for $HCrO_4^-$. The measured rate was independent of wavelength as judged by the results of several runs made at 287.5 mμ for which $\epsilon_{I_3^-} = 40{,}000$ M^{-1} cm^{-1}. With $[H^+]_0 = 0.0116$ M and $[I^-]_0 = 0.1000$ M, the average value of $k_1 = 4.0 \times 10^{-4}$ sec^{-1} at 287.5 mμ was essentially the same as that at 353 mμ, $k_1 = 4.1 \times 10^{-4}$ sec^{-1}. There is no effect due to light since a solution kept in the dark and measured infrequently gave the same rate constant as a solution left in the light beam with maximum slit width. Measurements were made with a Beckman DU spectrophotometer with a cell compartment thermostated to ±0.02 and ±0.1° on a long-term basis. For runs with $t_{1/2} > 450$ sec, measurements were made manually. For $t_{1/2}$ between 125 and 450 sec, a Beckman energy-recording adapter allowed direct readout on a strip-chart recorder. With appropriate mixing techniques, readings were obtained within 30 sec of initial mixing.

Stock solutions of $HClO_4$ and K_2CrO_4 were prepared weekly and stored under nitrogen. Appropriate quantities of $HClO_4$ and K_2CrO_4 were mixed in one flask and KI and any added reagents in a second flask; the solutions were rapidly mixed and samples placed in 1-cm quartz cells. Ionic strength was maintained at 0.130 M using $KClO_4$. All runs on which the rate constants are based were carried out under nitrogen-flush conditions. Doubly distilled water was boiled and cooled under a stream of prepurified N_2, and in subsequent handling N_2 was kept over the solutions as much as possible. Each run contained a control blank with K_2CrO_4 omitted. When necessary, the corresponding kinetic runs were corrected for O_2 oxidation using this control. Several additional runs were made by flushing solutions with air or O_2 to examine the effect of oxygen on the rate.

For comparison a number of runs were carried out using a vacuum-line technique. A degassing cell similar to that described by Kice[10] was filled with 1.00 ml of one reactant solution and 3.00 ml of the second reactant in separate compartments. The solutions were frozen at −80°, the cell was evacuated, and then 730 Torr of prepurified N_2 was allowed back into the cell. After thawing, the cell was refrozen and this cycle repeated three times. After temperature equilibration, the cell was removed from the line and

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(7) Relevant to this study are the equilibria $2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O$, $K = 98$ M^{-1}, and $H_2CrO_4 \rightleftarrows H^+ + HCrO_4^-$, $K_{11} = 4.1$ M at 25° and $\mu = 1.00$ M, after J. Y. Tong and R. L. Johnson, *Inorg. Chem.*, **5**, 1902 (1966), and J. Y. Tong, *ibid.*, **3**, 1804 (1964).

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tipped to mix the solutions which were then allowed to fill a 4-ml Photo-Volt quartz cell attached to a side arm.

Stoichiometry. The consumption of H^+ was measured in solutions of composition $[Cr(VI)]_0 \sim 10^{-2}$–10^{-3} M, $[H^+]_0 = 0.0458$ M, and $[I^-]_0 = 0.090$ M. Thiosulfate was used to remove I_3^-, followed by NaOH titration of H^+ remaining, proper allowance being made for OH^- consumed by Cr(III). A low-temperature ion-exchange method was used to identify the Cr(III) species. A column of Dowex 50W-X4, 50–100 mesh resin in the H^+ form was constructed in a condenser through which 0° water was circulated. A solution (50 ml) containing 5.12×10^{-3} M K_2CrO_4, 0.100 M $HClO_4$, and 4.5 M KI was allowed to react at 20° for 4 min. The product mixture was cooled and a sample placed on the column. The column was washed with 0.1 M $HClO_4$ for 1 hr to remove absorbed iodine, followed by elution with 1 M $HClO_4$ to remove any 2+ species. The fractions preceding the intense violet $Cr(H_2O)_6^{3+}$ band were analyzed spectrally at 260 mμ where $\epsilon = 5470$ M^{-1} cm^{-1} for $Cr(H_2O)_5I^{2+}$.[11] After removal of the $Cr(H_2O)_6^{3+}$ band, a small green band remained near the top of the column, undoubtedly a 4+ dimer of Cr(III).

Results

Stoichiometry. The stoichiometric production of iodine was verified spectrophotometrically for solutions containing $[HCrO_4^-]_0 = 1.4 - 1.6 \times 10^{-5}$ M at 353 mμ under conditions in which concomitant oxidation of I^- was negligible. Using values of $K_{dissoc} = 0.00115$[12] and $\epsilon_{353} = 26{,}400$ M^{-1} cm^{-1} for I_3^-,[13] values of $(\Sigma I_2)_\infty/[Cr(VI)]_0 = 1.50 \pm 0.03$ were found. The reaction stoichiometry requires 8 moles of H^+ per mole of CrO_4^{2-} consumed. After correction for the interference of Cr(III) in the titration of hydrogen ion remaining, values of $([H^+]_0 - [H^+]_\infty)/[Cr(VI)]_0 = 8.1 \pm 0.2$ were observed.

The ultimate Cr(III) product was identified as the hexaaquo species. In an experiment in which $[HCrO_4^-]_0 = 1.28 \times 10^{-2}$ M and $[H^+] = 0.5$ M, molar absorption coefficients of ϵ_{408} 16.1 and ϵ_{575} 13.6 were obtained (after removal of iodine), in good agreement with literature values of ϵ_{408} 16.0 and ϵ_{575} 13.6 for $Cr(H_2O)_6^{3+}$.[14] The question arises as to whether or not $Cr(H_2O)_5I^{2+}$ is a precursor of the hexaaquo ion, since $Cr(H_2O)_5I^{2+}$ aquates with a half-life of approximately 1 hr under the conditions used.[11] A 0° ion-exchange separation of a product solution originally containing $[HCrO_4^-]_0 = 5 \times 10^{-3}$ M was carried out. There was no spectral evidence of any iodochromium(III); 85% of the chromium was accounted for as $Cr(H_2O)_6^{3+}$. In addition, an appreciable quantity of a green, dimeric chromium(III) species was observed. However, it seems unlikely that any of this dimer would be produced in the kinetic runs where $[HCrO_4^-]_0 \sim 10^{-5}$.

Rate Law. Reaction rates were measured over the following ranges of initial concentrations: $[Cr(VI)]_0 = (0.35$–$4.5) \times 10^{-5}$ M, $[H^+]_0 = 0.010$–0.10 M, and $[I^-]_0 = 0.0050$–0.12 M. Under the reaction conditions, both hydrogen ion and iodide ion were present in large excess over the initial concentration of Cr(VI). Furthermore, $HCrO_4^-$ is the only significantly occurring Cr(VI) species, comprising 98% of ΣCr(VI) in a typical run. Plots of $\ln (A_\infty - A)$ *vs.* t were linear over one to two half-lives, indicating a first-order dependence on $[HCrO_4^-]$. The absorbance, A, of the solution is due primarily to the triiodide product. In all of the runs there occurred a systematic deviation from strictly first-order kinetics in the region of the second or third half-life. The slopes of the log plots increase, indicating an apparent zero-order dependence. The deviation occurred earlier in runs containing relatively higher $[I^-]$ and lower $[H^+]$. The first-order constants (obtained from the linear portion of the log plots, *i.e.*, in the first to second half-life) were independent of $[HCrO_4^-]_0$ in the range $(1.0$–$4.5) \times 10^{-5}$ M. At lower initial concentrations, values of k_{obsd} increased 10–20% as the log plots were curved in the first half-life. At higher initial concentrations the log plots were linear to approximately three half-lives. All rate constants reported here refer to data collected for $[HCrO_4^-]_0 > 1.5 \times 10^{-5}$ M, in which region the rate constants are independent of $[HCrO_4^-]_0$.

Runs carried out with the initial addition of the products, I_3^- and $Cr(H_2O)_6^{3+}$, showed that this deviation near the end of the reaction was not due to the buildup of the products. Concentrations of $[I_3^-]_0 = 8.4 \times 10^{-5}$ M and $[Cr(H_2O)_6^{3+}]_0 = 5.5 \times 10^{-3}$ M had no effect on the rate. Furthermore, the presence of dissolved oxygen is not responsible for the deviation. The same deviation was present both for runs in which great precaution was taken to minimize the presence of O_2 (vacuum-line runs) and for those in which O_2 was purposely bubbled into solution. A series of 27 independent runs involving 58 combinations of H^+ and I^- concentrations was made to establish the dependence on H^+ and I^-. The results are summarized in Table I. These data cannot be correlated by an $[H^+]^2[I^-]^2$ rate term, as suggested by eq 6, or by $k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2$ terms, as required by eq 5. Each of these rate dependences requires that a plot of $k_{obsd}/[H^+][I^-]$ *vs.* $[H^+][I^-]$ be linear. Such a plot of the data in Table I results in a meaningless scatter of all points corresponding to $[H^+]_0 > 2 \times 10^{-2}$ M. Since the rate laws in eq 5 and 6 are inadequate for correlating the data, more general rate laws were tested. Trial rate laws were of three different types. The first of these involved three simple terms in the rate law.

$$k_{obsd} = k_1[H^+]^{a_1}[I^-]^{b_1} + k_2[H^+]^{a_2}[I^-]^{b_2} + k_3[H^+]^{a_3}[I^-]^{b_3} \quad (7)$$

The combinations of exponents chosen are listed in Table II. A least-squares computer program was employed to obtain individual rate constants, k_1, k_2, k_3, which would result in a calculated first-order constant, k_{calcd}, in best agreement with values of k_{obsd} for the various runs.[15] Three criteria were employed for choosing among the rate laws. It was assumed that the best rate law would (i) have the smallest dispersion (s') between calculated and observed values of the first-order rate constant, (ii) show no trend in the signed differences between values of k_{calcd} and k_{obsd} over the range of concentrations, and (iii) involve only positive rate constants. Trial rate law V failed to satisfy criterion ii and trial rate laws II, IV, and VI failed to satisfy criterion iii. Trial rate law I best

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(15) $s' = 100s/x$ is the per cent dispersion in the first-order rate constant. $s = [\Sigma(k_{obsd} - k_{calcd})^2(x/k_{obsd})^2/(n - v)]^{1/2}$, where $x = 10^{-3}$ sec^{-1}, n = number of input values of k_{obsd}, v = number of independent variables (rate constants). The quantity x/k_{obsd} is a weighting factor employed to give equal weight to both large and small values of k_{obsd}. The value of x chosen is somewhat arbitrary, and it was shown that the results are independent of the value of x. Furthermore, the per cent dispersion, $100s/x$, is independent of the value of x.

Table I. Kinetic Data for the First-Order Reaction of $HCrO_4^-$ at 20.34° and $\mu = 0.130\ M$[a]

$10^2[\mathrm{H}^+]$, M	$10^2[\mathrm{I}^-]$, M	10^4k_{obsd}, sec^{-1}	10^4k_{calcd}, sec^{-1}	$10^2[\mathrm{H}^+]$, M	$10^2[\mathrm{I}^-]$, M	10^4k_{obsd}, sec^{-1}	10^4k_{calcd}, sec^{-1}
0.941	6.53	1.77	1.74	5.18	7.01	37.1	36.9
0.950	12.00	3.66	3.90	5.82	1.003	4.61	4.60
1.009	5.00	1.33	1.38	6.05	0.600	2.95	2.93
1.009	10.02	3.68	3.33	6.05	0.703	3.45	3.47
1.163	10.00	4.10	4.09	6.05	0.904	4.63	4.53
1.163	10.00	4.08	4.09	6.06	0.598	2.90	2.92
1.163	10.00	3.98	4.09	6.06	0.706	3.48	3.48
1.317	6.52	2.76	2.78	6.06	0.901	4.74	4.52
1.330	5.00	1.85	2.02	6.62	1.000	6.47	6.29
1.412	5.00	1.99	2.20	6.62	1.001	6.70	6.30
1.412	6.51	3.18	3.07	6.91	3.00	25.3	24.1
1.412	10.02	5.94	5.51	6.91	5.03	50.7	45.8
1.63	10.01	6.75	6.90	6.98	0.995	7.14	7.15
1.66	10.18	7.02	7.29	7.60	3.00	29.9	30.6
1.882	6.51	4.97	4.80	8.27	1.104	12.4	12.4
2.02	5.00	3.82	3.80	8.27	3.00	34.5	38.0
2.02	10.02	10.0	9.87	8.27	2.00	23.5	23.8
2.35	6.51	7.09	6.99	8.63	2.00	25.8	26.6
2.85	5.00	7.12	6.91	8.63	3.00	38.2	42.3
3.45	8.00	18.5	19.1	8.63	4.00	55.3	59.8
3.45	7.00	18.7	15.8	9.93	0.509	9.49	8.91
3.45	8.00	23.7	22.7	9.93	0.598	11.3	10.6
3.80	5.00	13.4	12.1	9.93	0.698	13.8	12.5
4.04	1.000	1.99	2.01	9.93	0.996	18.5	18.1
5.04	0.896	3.02	2.91	9.93	2.01	38.7	38.8
5.04	0.998	3.36	3.27	9.93	3.08	55.0	62.9
5.04	2.00	7.90	7.14	10.36	1.005	20.9	20.5
5.18	5.00	23.5	23.4	10.36	2.00	41.5	43.1
5.18	6.02	28.1	29.9	10.36	2.65	54.1	59.2

[a] $[HCrO_4^-]_0 = 1.5\text{–}2.0 \times 10^{-5}\ M$.

Table II. Trial Exponents for a Three-Term Rate Law[a]

Trial	a_1	b_1	a_2	b_2	a_3	b_3	s'[b]
I	1	1	2	2	3	1	6
II	1	1	2	2	3	2	26
III	1	1	2	1	3	2	13
IV	1	2	2	2	3	2	46
V	1	1	2	1	2	2	13
VI	1	1	2	1	1	2	12
VII	1	2	2	2	3	1	14

[a] Quantities a_1 and b_1 are defined by eq 7. [b] See ref 15.

satisfies criterion i and, accordingly, is judged to be the best rate law.

The second type of trial rate law involved an inverse $[\mathrm{I}^-]$ dependence in one term of a three-term expression. The k_2 term of trial rate law I and the k_3 term of trial rate law II were multiplied by $1/(k' + [\mathrm{I}^-])$. Values of k' were varied arbitrarily from 0.001 to 1.00. No minimum in s' was observed in this range. In both cases, the lowest deviation occurred for $k' = 1.00$, thus indicating that inverse $[\mathrm{I}^-]$ dependence is not involved. A third type of trial rate law involved the addition of one or more terms to trial rate laws I–VII. Since none of these resulted in values of $s' < 6$, rate laws of this type were not considered further. Trial rate law I remains the best choice

$$\frac{-\mathrm{d}\ln\,[\mathrm{HCrO_4^-}]}{dt} = k_1[\mathrm{H}^+][\mathrm{I}^-] + k_2[\mathrm{H}^+]^2[\mathrm{I}^-]^2 + k_3[\mathrm{H}^+]^3[\mathrm{I}^-] \quad (8)$$

with values at 20.34° and $\mu = 0.130\ M$ of $k_1 = 0.206 \pm 0.009\ M^{-2}\ \mathrm{sec}^{-1}$, $k_2 = 111 \pm 7\ M^{-4}\ \mathrm{sec}^{-1}$, and $k_3 = 154 \pm 3\ M^{-4}\ \mathrm{sec}^{-1}$. The values of k_{calcd} in Table I are based on these values.

The results above were obtained under nitrogen-flush conditions as described in the Experimental Section. In addition, several kinetic runs were made using the vacuum-line technique which further reduces the oxygen content of the solutions. The values of k_{obsd} thus obtained were in good agreement with values predicted from data obtained using nitrogen-flush conditions. Therefore, it appears that neither the form of the rate law nor the values of the individual rate constants are affected within experimental error by the presence of small amounts of oxygen. To further test this conclusion, deliberate introduction of oxygen into the reactant solutions was found to have no appreciable effect on the rate constants. The presence of oxygen does, however, increase the ultimate concentration of I_3^- produced, as expected. Under nitrogen-flush conditions, the increase in the value of A_∞ was small, and its effect was eliminated by a blank correction. The trial runs in which oxygen was deliberately added led to a particularly significant observation. Even after correcting values of A_∞ for I_3^- produced in control runs (no initial chromate), the values of A_∞ were larger than those expected on the basis of the initial concentrations of $HCrO_4^-$. Therefore, it is clear that the presence of one or more of the reaction intermediates induces the reaction of O_2 with I^- and H^+. This effect was as large as 23% when solutions containing 0.1 M I^- were flushed with oxygen. Under the kinetically important nitrogen-flush conditions, this catalytic behavior was small enough so as to be observable only at high iodide concentrations.

The dependence of k_{obsd} on ionic strength was determined by addition of KNO_3 as the inert electrolyte. Within experimental error, first-order rate constants were the same with KNO_3 or $KClO_4$ as the supporting electrolyte at the 0.130 ionic strength level. In Table

Table III. Effect of Ionic Strength on Values of k_{obsd}[a]

μ, M	10^4k_{obsd}, sec^{-1}	μ, M	10^4k_{obsd}, sec^{-1}
0.062	3.20	0.640	2.07
0.130	2.92	0.831	1.91
0.141	2.83	0.997	2.18
0.398	2.37	1.00	2.44

[a] Using KNO_3 as the neutral electrolyte at 20.34°.

III are shown the results of a series of runs carried out at $[HCrO_4^-]_0 = 1.68 \times 10^{-5}$ M, $[H^+]_0 = 0.0222$ M, and $[I^-]_0 = 0.0400$ M. Values of k_{obsd} decrease as ionic strength increases, go through a minimum at approximately 0.8 M, and then increase with a further increase in ionic strength. No change in values of k_{obsd} was noted for runs in which $NaNO_3$ was substituted for KNO_3.

The temperature dependences of k_{obsd} and of the individual rate constants, k_1, k_2, and k_3, were determined. At 10.37°, average rate constants based on seven independent runs are: $k_1 = 0.049 \pm 0.007$ M^{-2} sec^{-1}, $k_2 = 63.5 \pm 7$ M^{-4} sec^{-1}, and $k_3 = 108 \pm 4$ M^{-4} sec^{-1}. At 29.67°, average rate constants based on nine independent runs are: $k_1 = 0.253 \pm 0.032$ M^{-2} sec^{-1}, $k_2 = 201 \pm 23$ M^{-4} sec^{-1}, and $k_3 = 241 \pm 15$ M^{-4} sec^{-1}. The corresponding activation parameters for the k_2 and k_3 terms are: $\Delta H_2^{\ddagger} = 9.7 \pm 1.5$ kcal/mole and $\Delta S_2^{\ddagger} = -16 \pm 6$ eu, $\Delta H_3^{\ddagger} = 6.3 \pm 1.0$ kcal/mole and $\Delta S_3^{\ddagger} = -27 \pm 3$ eu. The plot of log (k_1/T) *vs.* $1/T$ was sufficiently nonlinear that no meaningful values for $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ could be obtained.

Effect of Added Species. Several runs were made in the presence of added halide ions. There was no effect on k_{obsd} at concentrations of Cl^- up to 0.19 M, or of concentrations of Br^- up to 0.054 M. At very high ionic strength, Cl^- does have a modest effect on the rate. The value of k_{obsd} in 1.42 M NaCl is 2.3 times that in 1.42 M $NaNO_3$. Several runs containing added $MnCl_2$ were made; the results are shown in Table IV.

Table IV. The Effect of Added Mn(II) Ion on the Rate of Reaction at 20.34° and $\mu = 0.130$ M[a]

$10^2[H^+]$, M	$10^2[I^-]$, M	$10^2[Mn(II)]$, M	10^4k_{obsd}, sec^{-1}
2.33	7.06	0.162	7.52
1.16	10.00	0.448	4.16
1.16	10.00	1.023	4.10
1.74	6.01	3.46	3.91

[a] $[HCrO_4^-]_0 = 1.69 \times 10^{-5}$ M.

The corresponding values of k_{obsd} obtained in the range $[Mn^{2+}]_0 = 0.0016$–0.035 M are within experimental error of first-order rate constants calculated from the rate law. There was no indication that Mn^{2+} retards the reaction, nor was there any evidence that MnO_2 replaced I_3^- as the oxidized product.

A brief examination of the effects of added organic radical scavengers was made. Benzaldehyde, in concentrations up to 8.7×10^{-3} M, had no effect on the rate of reaction or on the values of A_∞ and did not affect the extent of apparent zero-order deviation in the first-order plots. Addition of allyl acetate in concentrations up to 9.2×10^{-3} M resulted in an 18% acceleration in the rate.

Discussion

The rate law found in this study, eq 8, includes terms not contained in either of the previously reported rate expressions, eq 5 and 6. The lack of agreement with the result in eq 5 is not surprising in view of the fact that Edwards[16] has shown that Taylor and Beard's data may also be interpreted by the additional inclusion of the terms $k_c[H^+]^2[I^-]$ and $k_b[H^+][I^-]^2$. However, there is no apparent explanation for the fact that Howlett and Sarsfield were unable to find a dependence lower than second order for H^+ and I^-. The $[H^+]^3[I^-]$ term in the present rate law arises because our data extend to $[H^+]_0 = 0.10$ M, whereas the highest concentration reported by Howlett and Sarsfield is $[H^+]_0 = 0.050$ M. This is simply another demonstration of the fact that many complex reactions do not have unique rate expressions, but rather that these expressions are valid only in the concentration ranges examined. Because of the difference in the rate laws, no quantitative comparison of the magnitude of the rate is possible. Initial rates calculated from data obtained in this study are one to two times greater than corresponding values from ref 6, in which rate data are based on $-d[I^-]/dt$ (M min^{-1}) at 25°.

Presumably, each term in the rate law corresponds to a separate pathway for reaction. Possible steps leading to the activated complex for the k_2 path are

$$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4 \qquad (9)$$

$$H_2CrO_4 + I^- \rightleftharpoons ICrO_3^- + H_2O \qquad (10)$$

$$ICrO_3^- + H^+ + I^- \longrightarrow \text{rate determining} \qquad (11)$$

It should be made clear that the kinetic data do not allow any choice to be made in the relative order of addition of H^+ and I^-, nor do they discriminate between attack by iodide at the Cr center, as opposed to attack at an oxygen center. The species $I\text{-}CrO_3^-$ seems a likely intermediate by analogy with the known $Cl\text{-}CrO_3^-$ species.[7,17] That the soft nucleophile I^- can have an appreciable reactivity at Cr(VI) is evidenced by the catalysis of the hydrolysis of $Cr_2O_7^{2-}$ by thiourea, also a soft nucleophile.[18] The pathways for the k_1 and k_3 terms are presumably similar. Except for the altered composition of the activated complex, there are no data which bear on any specific differences which may occur.

Turning now to a consideration of the immediate products of the rate-determining step and the nature of subsequent steps, the Westheimer mechanism would be (for the k_2 step)

$$ICrO_3^- + H^+ + I^- \longrightarrow Cr^{IV} + I_2 \quad \text{slow} \qquad (12)$$

$$Cr^{IV} + Cr^{VI} \longrightarrow 2Cr^{V} \qquad (13)$$

$$Cr^{V} + I^- \longrightarrow Cr^{III} + HOI \qquad (14)$$

$$HOI + H^+ + I^- \longrightarrow I_2 + H_2O \qquad (15)$$

A two-electron transfer in the slow step, eq 12, appears most reasonable, although a three-electron process, similar to that proposed by Haight for the Cr(VI)–S(IV) system,[3c] is also possible. Far less likely are the four-electron transfer producing Cr(II) and the one-electron transfer corresponding to a rate-limiting change

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(16) J. O. Edwards, *Chem. Rev.*, 50, 455 (1952).

(17) G. P. Haight, D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, 3, 1777 (1964).

(18) B. Perlmutter-Hayman and M. A. Wolff, *Can. J. Chem.*, 43, 2913 (1965).

$Cr(VI) \rightarrow Cr(V)$. There is considerable evidence to show that it is reduction to the Cr(IV) state, involving a change from fourfold to sixfold coordination, which is rate limiting.[3a,b]

Any complete mechanism written must account for the following observations: (a) there is an apparent increase in rate after one to two half-lives, (b) the Cr(VI)–I^- system induces the $O_2 + H^+ + I^-$ reaction, and (c) added Mn^{2+} does not retard the reaction, nor does it change the deviation toward zero-order kinetics after one to two half-lives. The mechanism shown in steps 12–15 fails to account for observation a and can explain observation b only by assuming that Cr(V) or Cr(IV) reacts with O_2, for which there is no independent evidence. Mn^{2+} retards Cr(VI) oxidation of organic compounds either by the formation of unreactive MnO_2 or by catalyzing the disproportionation of Cr(IV) to Cr(III) and Cr(VI).[19] Specifically, Mn(II) eliminates reaction 13 by diverting Cr(IV) as shown in eq 16. The same diversion must then

$$Cr^{IV} + Mn^{II} \longrightarrow Cr^{III} + Mn^{III} \qquad (16)$$

occur in the present situation since $[Mn^{2+}]_0/[Cr(VI)]_0 \sim 10^3$, which is considerably higher than the same ratio for the organic oxidations. However, the fate of Mn(III) in iodide solutions is very likely to be

$$Mn^{III} + I^- \longrightarrow Mn^{II} + I\cdot \qquad (17)$$

If I· (actually present as I_2^- [20]) is subsequently oxidized by Cr(VI), no change in rate would be expected, since a total of two Cr(VI)'s are consumed each time the rate-determining step 12 takes place. The fact that the production of I· in the presence of added Mn^{2+} does not affect the reaction rate suggests that a better formulation of the mechanism might be eq 12, followed by

$$Cr^{IV} + I^- \longrightarrow Cr^{III} + I\cdot \qquad (18)$$

$$Cr^{VI} + I\cdot \longrightarrow Cr^{V} + HOI \qquad (19)$$

$$(\text{or, } Cr^{VI} + I_2^- \longrightarrow Cr^{V} + I_2)$$

$$Cr^{V} + I^- \longrightarrow Cr^{III} + HOI \qquad (20)$$

This sequence places I^- in competition with Cr(VI) for reaction with Cr(IV). Under the present conditions in which $[I^-]_0/[Cr(VI)]_0 \sim 10^3$, reaction 18 may very well predominate over reaction 13. There is ample evidence that Cr(IV) is an effective one-electron oxidant, both thermodynamically[21] and kinetically.[3a,b,19,22] The steps involving formation of iodine radical species are consistent with the induction of the $O_2 + H^+ + I^-$ reaction. Boyer and Ramsey present convincing evidence that I_2^- does induce the O_2 oxidation of I^- in acidic, aqueous solution.[20] Further support for the existence of reaction 18 is derived from a comparison of the results with respect to retardation of the reaction by added iodine. Howlett and Sarsfield report that added I_2 retards the reaction, with a concomitant change from first- to second-order dependence on Cr(VI). The retardation was ascribed to a reversibility of reaction 12. No such effect was observed in the present study. This lack of agreement may well arise from the fact that under the present conditions in which $[I^-] \gg [I_2]$, Cr(IV) reacts with I^- to the exclusion of all other species, including I_2. In summary it seems likely that if reaction sequence 12–15 occurs at all in the chromium(VI)–iodide reaction, it is either partially or entirely replaced by sequence 12, 18–20 under conditions where the initial concentration of $HCrO_4^-$ is very low. Roček and Radkowsky have presented evidence recently that the classical sequence 12–15 is not operative in the chromium(VI) oxidation of cyclobutanol.[22]

Although the suggested mechanism accounts for observations b and c, it fails to explain observation a, the eventual deviation toward a zero-order dependence on $HCrO_4^-$. This deviation was quite reproducible and was unaffected by oxygen and added Mn^{2+}. We have considered, but have ruled out, the possibility of a separate reaction path which is zero order in $HCrO_4^-$ Such a path would involve only H^+, I^-, and solvent in the activated complex in which case no reasonable electron transfer can occur. The apparent deviation could result from the disappearance of more than two $HCrO_4^-$ per slow step, an effect that would be produced by reaction of an intermediate with $HCrO_4^-$. Addition of steps 21 and 22 would account for the increased consumption of $HCrO_4^-$ by virtue of the extra iodine radical species generated in step 21. This reaction

$$Cr^{V} + I^- \longrightarrow Cr^{IV} + I\cdot \qquad (21)$$

$$2I\cdot \longrightarrow I_2 \qquad (22)$$

sequence would not be expected to make a major contribution to the over-all production of iodine, since the recombination in step 22 is undoubtedly very efficient.

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(20) M. H. Boyer and J. B. Ramsey, *ibid.*, **75**, 3802 (1953).

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