AN ABSTRACT OF THE THESIS OF

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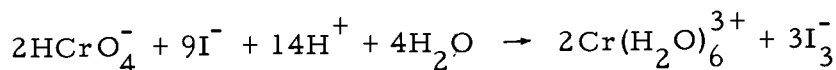
Title: A Kinetic Investigation of the Mechanism and Intermediates

of the Chromium(VI)-Iodide Reaction

Abstract approved: *Redacted for Privacy*
                              James Krueger

The kinetics of the reaction between $HCrO_4^-$ and I^- in acid solution were studied spectrophotometrically. The stoichiometry of the reaction is:

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

The reaction was first-order in $HCrO_4^-$, and the H^+ and I^- dependencies were determined from their effect on the pseudo-first-order rate constant. The rate law is:

$$\text{Rate} = [HCrO_4^-](k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-])$$

Each term contributed at least 60% of the reaction pathway in certain concentration ranges. The measured k_i values are: $k_1 = 0.206 \ M^{-2}sec^{-1}$, $k_2 = 111 \ M^{-4}sec^{-1}$, and $k_3 = 154 \ M^{-4}sec^{-1}$ at 20.34° at ionic strength $= 0.130 \ M$. The concentration ranges of the reactants were $[I^-]$, $0.5 = 12.0 \times 10^{-2} \ M$; $[H^+]$, $0.95 - 10.36 \times 10^{-2} \ M$; and $[HCrO_4^-]$, $0.325 - 4.5 \times 10^{-5} \ M$.
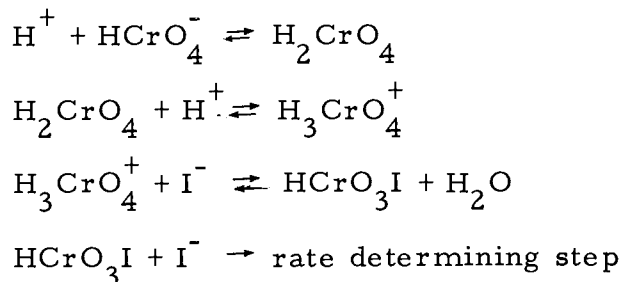
The reaction was found to be less than first order in $HCrO_4^-$ at concentrations below 1.0×10^{-5} M. This deviation appears to be due to a zero-order reaction in $HCrO_4^-$ that competes with the first-order term. Neither the reaction products nor the dissolved oxygen remaining in the solutions appeared to be the source of this deviation. We propose that it is due to a reaction intermediate such as I_2^-.

Chloride and bromide ions were found not to catalyze the reaction when present in concentrations of 0.19 M and 0.05 M, respectively. Mn(II) ion and benzaldehyde did not divert any of the chromate oxidation from the iodide ion and did not influence the reaction rate. Allylacetate appeared to increase the rate of reaction.

Temperature studies of the reaction were made at 10.37°, 20.34° and 29.67°. The measured activation parameters for the k_2-step are: $\Delta H^{\ddagger} = 9.6$ Kcal/mole $\Delta S^{\ddagger} = -16$ e.u. and for the k_3-step: $\Delta H^{\ddagger} = 6.3$ Kcal/mole $\Delta S^{\ddagger} = -27$ e.u. The temperature plot for the k_1-term was non-linear and its activation parameters could only be estimated.
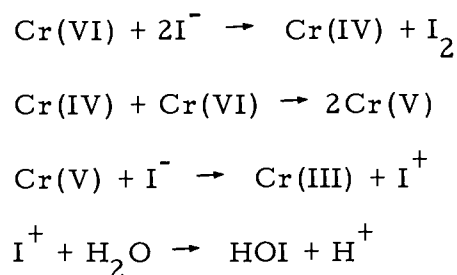
In the presence of added molecular oxygen, the reaction was found to produce more iodine than could be accounted for by the combined reactions of $HCrO_4^- + I^-$ and $H^+ + O_2 + I^-$. An intermediate (I_2^-) of the $HCrO_4^- + I^-$ reaction was assumed to be responsible for this catalytic effect on the $H^+ + O_2 + I^-$ system. This latter reaction did not affect the kinetics of the $HCrO_4^- + I^-$ reaction since the reaction rate was not dependent on O_2 content.

The mechanism for the reaction must contain three independent pathways to be consistent with the rate law. The k_2-term pathway is representative of the mechanisms.
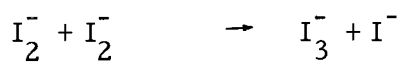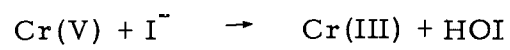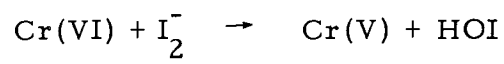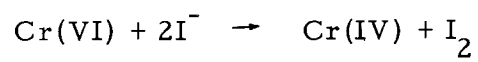
$$H^+ + HCrO_4^- \rightleftharpoons H_2CrO_4$$

$$H_2CrO_4 + H^+ \rightleftharpoons H_3CrO_4^+$$

$$H_3CrO_4^+ + I^- \rightleftharpoons HCrO_3I + H_2O$$

$$HCrO_3I + I^- \rightarrow \text{rate determining step}$$

The k_1-term would be an attack of a single I^- upon the H_2CrO_4. The k_3-term pathway could be H^+ adding to the $HCrO_3I$. The resulting complex could react in a slow step.

The Westheimer mechanism

$$Cr(VI) + 2I^- \rightarrow Cr(IV) + I_2$$

$$Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$$

$$Cr(V) + I^- \rightarrow Cr(III) + I^+$$

$$I^+ + H_2O \rightarrow HOI + H^+$$

cannot account for our observation that Mn(II) ion does not retard the rate of reaction. It has been established that $Cr(IV) + Mn(II) \rightarrow Cr(III) + Mn(III)$ competes with the Cr(IV) - Cr(VI) reaction. Therefore added Mn(II) ion should decrease the rate of reaction in Cr(VI) by a factor of two. Since $[I^-]/[Cr(VI)]$ is greater than 400 in this study, the Westheimer mechanism may not hold. A mechanism consistent with the observed kinetic data is:

$$Cr(VI) + 2I^- \rightarrow Cr(IV) + I_2$$

$$Cr(IV) + I^- \rightarrow Cr(III) + I\cdot$$

$$I\cdot + I^- \rightleftarrows I_2^-$$

$$Cr(VI) + I_2^- \rightarrow Cr(V) + HOI$$

$$Cr(V) + I^- \rightarrow Cr(III) + HOI$$

$$I_2^- + I_2^- \rightarrow I_3^- + I^-$$

A Kinetic Investigation of the Mechanism and Intermediates
of the Chromium(VI)-Iodide Reaction

by

Dennis Charles Gaswick

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A KINETIC INVESTIGATION OF THE MECHANISM AND INTERMEDIATES OF THE CHROMIUM(VI)-IODIDE REACTION

INTRODUCTION

The redox reaction of chromate ion and iodide ion in acid solution is a well known analytical method for standardizing thiosulfate solutions (43). Also, in kinetic studies of redox reactions of chromate with reducing agents, the behavior of iodide ion has been used in interpreting the intermediate species of chromium that are produced. However, the kinetics of the chromate redox reaction with iodide ions have not been thoroughly studied. In his 1949 review Westheimer (67) could only quote the rate law Beard and Taylor (6) presented in 1927 for this reaction. Westheimer (67, p. 443) then stated, "But at present little more [than the rate law] can be said about this highly important reaction." Since 1949 no papers have appeared on the kinetics of the chromate-iodide reaction until a recent paper by Howlett and Sarsfield (36). The reason for this neglect could be that the kinetics of the reaction are complex, and no simple interpretation is readily accessible.

The review article by Westheimer (67) is a good summary of the kinetic data for the chromic acid redox reactions known up to that time. He has listed the theoretical ways in which chromium (VI) can react with reducing agents to arrive at the final product of

chromium(III). The various steps are considered with the known

kinetics and other chemical data. A general mechanism for a two-

electron transfer step is developed. This development will be

expanded later. Wiberg (68) and Stewart (57) have also reviewed

redox reactions involving chromic acid.

The Chromate Equilibria

The chromate system in an acidic aqueous solution has four

separate species which may be present. They are the monomers

CrO_4^{2-}, $HCrO_4^-$, H_2CrO_4 and the dimer $Cr_2O_7^{2-}$. The following

equilibria must be taken into consideration to obtain the concentrations

of these various forms.

(1) $\quad H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \qquad K_1 = 4.16 \text{ M}$

(2) $\quad HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \qquad K_2 = 3.0 \times 10^{-7} \text{ M}$

(3) $\quad 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad K_{22} = 98 \text{ M}^{-1}$
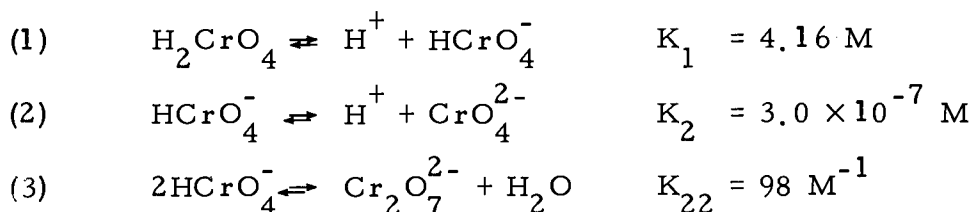
The ideal system to study kinetically would have only one of the

species present so that the various key values would not have to be

known with great accuracy. The K_2 value has been determined by

Howard, Nair and Nancollas (35). The CrO_4^{2-} anion is present in a

3.0×10^{-5} M acid solution as only 1% of the $\Sigma[Cr(VI)]$ when

$\Sigma[Cr(VI)]$ is equal to the sum of the concentrations of all the

chromate species. The K_{22} constant has been determined by Tong

and King (59, 62) who reported a value 98 M^{-1}. For the concentration of $HCrO_4^-$ below 1×10^{-4} M the $Cr_2O_7^{2-}$ form accounts for 1% or less of the $\Sigma[Cr(VI)]$.

The value of K_1 is the most controversial of the three equilibrium values. The values at 25° for this constant with the ionic strength, μ, used for the measurement are listed below.

	K_1, M	μ, M
Neuss and Rieman (50)	0.18	0.16
Tong and King (62)	1.2	1.00
Tong (59)	4.16	1.00
Tong and Johnson (60)	4.1	1.00
Bailey et al. (4)	10	→ 0
Shevchenko, Shilin, and Zhdanov (56)	1.2	1.00
Haight, Richardson, and Coburn (30)	5	1.00

The value by Neuss and Rieman is considered unlikely in view of the other values measured for this equilibrium. Tong and King (62) first published the value of 1.2 M for this equilibrium, but later interpretation by Tong (59) gave the value 4.16 M. In a different study, using a slightly different technique, Tong and Johnson (60) obtained the value 4.1 M. The measurement by Haight (30) was close to these values. Shevekenko et al. (56) used distribution measurements

of chromate solutions between an organic phase and water. Their value is very close to the value by Tong and King. The value of 4.16 M, measured by Tong, is considered to be the best choice. His work is concerned mainly in measuring the K_1 value, and he has obtained consistent results in two different studies.

The only oxidation states of chromium that are stable in an aqueous solution are the +6, +3 and +2 states. The +2 state is not directly involved in this study and will not be discussed further. The +6 state has been previously described, and it has a coordination number of four. It will be represented with the symbol Cr(VI) in reaction sequences when only the oxidation state is important. The +3 state will be considered to be the hexaquochromium(III) ion, represented by Cr(III), unless otherwise stated. The water ligands are considered to be inert and cannot be displaced easily by other potential ligands in the solution.

In reducing Cr(VI) to Cr(III), the chromium can pass through the oxidation states of +5 and +4. These states are very reactive in acidic solution, and they can only be studied by indirect methods. The actual forms of these ions in solutions are assumed to be $HCrO_4$ and $Cr(H_2O)_6^{4+}$, respectively (61). The coordination change from four to six appears to take place between these two oxidation states. These two species will be represented by Cr(V) and Cr(IV)

since the oxidation states are normally more important in the following discussions.

The Iodine Species

Iodine in aqueous solutions of KI can be present as either I_2 or I_3^- :

$$(4) \qquad I_2 + I^- \rightleftharpoons I_3^- \qquad K = 870 \ M^{-1}$$
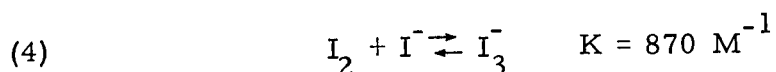
This equilibrium has been studied by various researchers, (3, 15, 16, 37, 38, 48, 71) and these works are summarized by Mironov and Lastovkina (48). A $\Delta G = -3.9$ Kcal/mole at 25° was obtained in all cases; however, the ΔH and ΔS dependencies were not in agreement. The value, 870 M^{-1}, measured by Kutzin and Gilbert (38) at 20° with ionic strength = 0.100 M, and $HClO_4$ = 0.01 M, is used in this study since these conditions are very close to the reaction conditions involved here. Their K measurements are in agreement with the latest measurements by Mironov and Lastovkina (48).

Two iodine species must be considered as reaction inter-mediates. In a two electron transfer the iodide ion would go to a plus one state represented by HOI. This species is a weak acid (49), $K_a = 4.5 \times 10^{-13}$ M, and it reacts rapidly with an iodide ion to give iodine. In a one electron step, an iodine atom would be produced, and there is evidence that in an iodide ion solution this atom would

form the diiodide ion (12, 29).

$$(5) \qquad I\cdot + I^- \rightleftarrows I_2^-$$

$$(6) \qquad I_2^- + I_2^- \rightarrow I_3^- + I^-$$
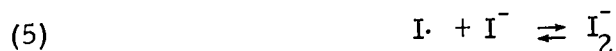
Two diiodide ions can react to produce a triiodide ion.

Westheimer Mechanism for Induced Reactions

Chromic acid redox reactions involving a two electron transfer step have been suggested in several studies with various reducing agents. Examples of this type of reaction are the oxidations of secondary alcohols (66, 67), benzaldehyde (69, 29), AsO_3^{3-} (47) and H_3PO_3 (52). The reaction which has recieved the most kinetic attention is the oxidation of a secondary alcohol to a ketone. Westheimer (66, 67) dealt with a general mechanism for this type of reaction, and it will be redeveloped briefly here.

If the two electron reducing agent is represented by the symbol H_2A, i.e. secondary alcohol, the following mechanism is favored by Westheimer. The hydrogen ions on H_2A are used only to indicate the oxidation state of A, and no attempt has been made to balance them.

$$(7) \qquad Cr(VI) + H_2A \rightarrow Cr(IV) + A$$

$$(8) \qquad Cr(VI) + Cr(IV) \rightarrow 2Cr(V)$$

$$(9) \qquad Cr(V) + H_2A \rightarrow Cr(III) + A$$
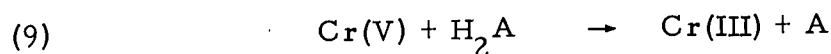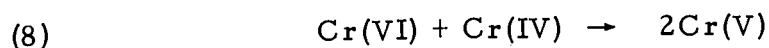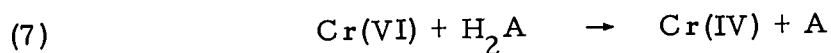
The H_2A changes only by a two electron step to form the product A.

A point of interest is the reaction of Cr(IV) with Cr(VI), instead of a

reaction of Cr(IV) with H_2A. The intermediate Cr(IV) allows for

another reaction pathway, Step (8), for the Cr(VI) in addition to the

original reaction with H_2A, Step (7).

This mechanism is based upon induced reactions observed in

many chromate reductions. In the study of the chromate-secondary

alcohol reaction (66) Mn(II) ion was added to the reaction, and not

only was the Mn(II) ion oxidized to MnO_2, but the rate of the chromate-

alcohol reaction was decreased by one-half. However, with Mn(II)

added to either a solution containing the chromate species or one con-

taining the alcohol, no reaction was observed. This type of behavior,

in which an added reducing agent is oxidized during the main reaction

but not by either of the original reactants, is called an induced reac-

tion. The induction factor, I. F. , is the ratio of the induced product

equivalents to the number of product equivalents from the initial

reaction. In the particular case of the secondary alcohol with added

Mn(II) ion the I. F. is:

$$\text{I. F.} = \# \text{ equiv. of } MnO_2 / \# \text{ equiv. of ketone.}$$

As the initial concentration of Mn(II) ion is increased in relation to

the alcohol concentration, the I. F. approaches a value of 0.5 but does

not appear to ever go beyond this value. The chromate ion removes

one electron from Mn(II) for every two electrons it takes from the

secondary alcohol.

There are other induced reactions observed during the reduction of the chromate ion. A well-known example is the oxidation of iodide ion by chromate in the presence of Fe(II) (7). In this reaction the induction factor is equal to two. For every Fe(III) ion produced, the reaction produces one molecule of iodine. The I. F. values of 0.5 and 2.0 are the main ones that have been observed. The Ce(III) ion has also been used in place of Mn(II), but normally the Ce(III) or Ce(IV) will react with a reactant or product. Therefore, this system has not been well studied. The reactions with benzaldehyde (28) and phenyl-t-butylcarbinol (32) are two in which Ce(III) can be used. It gives the same behavior noted for the Mn(II) ion. Oxygen also becomes absorbed during some chromate redox reactions, but it normally does not result in a definite I. F. value. Induced reactions involving oxygen either appear in cases where an intermediate of Cr(II) is possible (42), or, more normally, where the intermediates of the reducing agent rather than a chromium intermediate can react with the oxygen (64, 65).

The Westheimer mechanism makes use of the induction factors found for Mn(II), Ce(III) and iodide ions. The Mn(II) and Ce(III) are used as scavengers for the Cr(IV) produced from the initial reaction of $Cr(VI) + H_2A$.

(10) $Cr(VI) + H_2A \rightarrow Cr(IV) + A$

(11) $Cr(IV) + Mn(II) \rightarrow Cr(III) + Mn(III)$
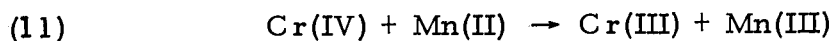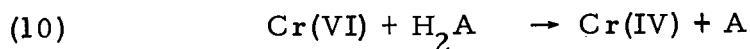
The Mn(II) loses one electron for every two lost by H_2A, and the induction factor equals 0.5. The reaction:

(12) $Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$
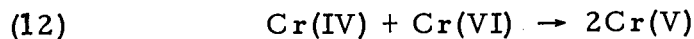
cannot compete with the Mn(II) for the Cr(IV) intermediate. The rate of Cr(VI) disappearance is thereby decreased by a factor of two. This rate decrease was observed in the secondary alcohol reaction with added Mn(II) ion as previously stated. The iodide ion, on the other hand, is taken to be reactive only with the Cr(V) species. Its induction factor of two can be explained if it does not react with Cr(IV). The H_2A reduces the Cr(VI) to Cr(IV) which in turn reacts with a Cr(VI) to give two Cr(V) species, Step (12). These two Cr(V) species represent a four electron change going to the product Cr(III). If the reaction $Cr(V) + H_2A$ is assumed to be slow compared to the $Cr(V) + I^-$ reaction, then the iodide ions lose four electrons for every two lost by H_2A. The induction factor is equal to $4/2 = 2.0$ as is observed in the reaction with As(III) and other reductants (24, 7, 46).

Alternate Mechanism

An alternate mechanism which can be used to explain the kinetics of chromate and a two electron reducing agent is as follows:

(13) $\qquad Cr(VI) + H_2A \rightarrow Cr(IV) + A$

(14) $\qquad Cr(IV) + H_2A \rightarrow Cr(III) + HA\cdot$

(15) $\qquad HA\cdot + Cr(VI) \rightarrow Cr(V) + A$

(16) $\qquad Cr(V) + H_2A \rightarrow Cr(III) + A$
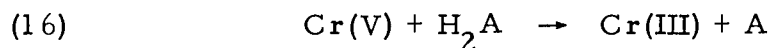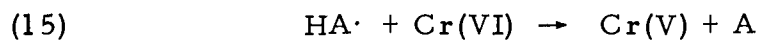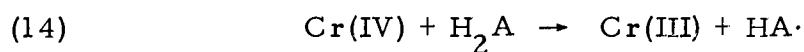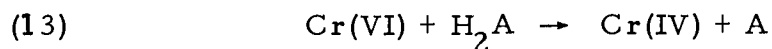
The main difference in the mechanisms proposed is the third step in which $Cr(VI)$ is reduced to $Cr(V)$. Westheimer (67) used $Cr(IV)$ for the step, (8), and this mechanism involves the $HA\cdot$ intermediate, Step (15). The question is whether $Cr(IV)$ reacts faster with $Cr(VI)$ or with H_2A. If the $Cr(VI)$ concentration is made low enough $[H_2A]$ / $[Cr(VI)] \sim 100$, then Reaction (14) could take place. If the $Cr(IV)$ intermediate is not selective in this reaction, the higher concentration of H_2A might divert the $Cr(IV)$ in this alternative mechanism.

A study by Wiberg and Richardson (70) has indicated that this latter mechanism is the more probable one in the oxidation of triphenylacetaldehyde with chromic acid. If the aldehyde forms a complex with $Cr(VI)$, the oxidation produces the expected acid product, triphenylacetic acid. However, an intermediate valence state of chromium produced a cleavage product, triphenylcarbinol, in a yield of 24%. This result can be best explained by having the cleaved product result from the reaction of $Cr(IV)$ with the aldehyde. This reaction produces an organic radical which then reacts with $Cr(VI)$.

Westheimer, Hampton and Leo (32) also studied the cleavage of an organic molecule by intermediate valence states of chromium.

They used the molecule phenyl-t-butylcarbinol as the reducing agent, and made a quite thorough study of the reaction products versus the initial chromium(VI) concentration. Again the uncleaved product, phenyl-t-butylketone, was assumed to be produced by the Cr(VI)-Cr(IV) step and the cleavage product to be produced by a chromium intermediate. The assumption made in this study was that Cr(V) reacts to produce the cleavage product, benzoic acid or benzaldehyde. This appeared to be an arbitrary choice. In some experiments up to 67% of the product was the cleavage product, although in most cases it was under 50%. The Westheimer mechanism was used to explain the results with two-thirds of the electrons involved in the Cr(V)-Cr(III) step. However, it was also stated that the radical mechanism could account for most of the data, except those experiments producing over 33% of the cleavage product. In the latter calculation the assumption was made that Cr(V) produced uncleaved product. This study did not give a clear cut choice in mechanisms, although it probably gives greater support to the Westheimer mechanism.

A recent paper questioning the Westheimer mechanism as a general scheme has been published by Roček and Radkowsky (54). Rocek has studied the redox reaction of cyclobutanol with chromate. He found that the main product was the expected ketone, but that in addition, the cleavage product $HOCH_2CH_2CH_2CHO$ was also obtained. In order to determine which oxidation state of chromium was producing

the cleavage product, cyclobutanol was added to the Cr(VI)-V(IV)

reaction. Espenson (24) has shown that the mechanism for the V(IV)-

Cr(VI) reaction is probably:

(17) $Cr(VI) + V(IV) \rightleftharpoons Cr(V) + V(V)$ equil.

(18) $Cr(V) + V(IV) \rightarrow Cr(IV) + V(V)$ r. d. s.

(19) $Cr(IV) + V(IV) \rightarrow Cr(III) + V(V)$ fast
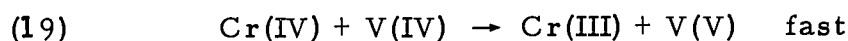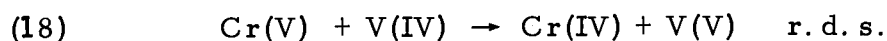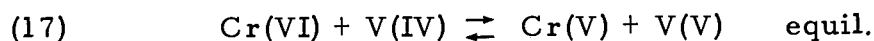
Since both Cr(IV) and Cr(V) are present, the cleavage product of

cyclobutanol should be observed. If the product arises from the Cr(V),

then the mechanism of the Cr(VI)-V(IV) reaction should be affected.

The Cr(V) + cyclobutanol reaction will compete for the Cr(V) produced

in the equilibrium step, (17), and the reaction rate should be increased.

However, if the Cr(IV) species produces the cleavage product, the

addition of cyclobutanol should make no difference in the rate law

observed. The cleavage product was observed in this induced reaction

and the reaction rate of Cr(VI)-V(IV) was unchanged. The cyclobutanol

cannot react rapidly with Cr(V) since it does not compete for this

intermediate over the relatively slow reaction of Cr(V) + V(IV),

Step (18). It must, in fact, react rapidly with Cr(IV) in order to

compete successfully with the fast step of Cr(IV) + V(IV), Step (19).

The mechanism proposed by Roček (54) was:

(20) $Cr(VI) + V(IV) \rightleftharpoons Cr(V) + V(V)$ equil.

(21) $Cr(V) + V(IV) \rightarrow Cr(IV) + V(V)$ r. d. s.

(22) $Cr(IV) + C_4H_7OH \rightarrow Cr(III) + R\cdot$

(23) $\qquad$ R· + V(V) $\qquad$ → HOCH$_2$CH$_2$CH$_2$CHO + V(IV)
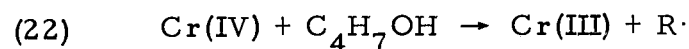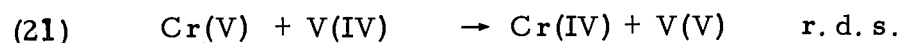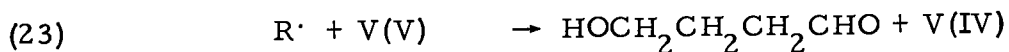
This study was limited to cyclobutanol, but Roček suggested that

preliminary studies with other reducing agents, isopropyl alcohol,

primary alcohols, as well as aldehydes, exhibited similar behavior.

The results of these latter studies have not been published. If they

do show similar results, the Westheimer mechanism and the induced

reaction will have to be restudied.

The Estimated E^o Values for Chromium Intermediates

The oxidation potentials, E^o, of the chromium intermediate

states, Cr(V) and Cr(IV), are not directly measureable. An estimate

of these values is given in the review by Westheimer (67). The same

method has been employed here to obtain the values except that the

more recent values of the measured E^o are used. In Westheimer's

estimations and in the recalculations done here, the effect of hydro-

gen ion concentration is not taken into account. In most studies the

acid concentration is roughly the same, and so this omission may

not cause much error. However, this omission should not be for-

gotten.

The potential of the Cr(VI)-Cr(V) couple is based on the

equilibrium step in the reaction between Cr(VI) and Fe(II). The

Fe(II)-Fe(III) couple is equal to 0.77 v., and the equilibrium

(24) $\qquad$ Cr(VI) + Fe(II) $\rightleftharpoons$ Cr(V) + Fe(III)
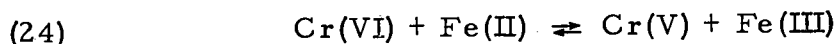
is assumed to be 99% to the right. The calculated value for the

Cr(VI)-Cr(V) couple is $E^o \leqslant 0.65$ v. Westheimer based his estimate

of E^o of the Cr(IV)-Cr(III) couple on the induced reaction of Mn(II)

caused by the Cr(IV). However, it has been shown by Tong and King

(61), that the equilibrium

(25) $$Ce(IV) + Cr(III) \rightleftharpoons Cr(IV) + Ce(III)$$
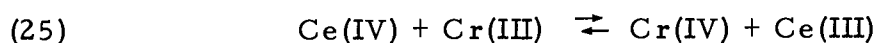
is established in the oxidation of Cr(III) to Cr(VI). Based on this

equilibrium and using the above procedure, an $E^o \geqslant 1.73$ v. can be

calculated. How much greater the E^o value is than 1.73 v. is not

known. From the values in Equations (27), and (31), the E^o values

for the following reaction couples can be calculated by using the

relationship $\Delta G^o = -nFE^o$.

(26) $\qquad$ Cr(VI) + 3e $\rightarrow$ Cr(III) $\qquad$ $E^o = 1.33$ v.

(27) $\qquad$ Cr(VI) + e $\rightarrow$ Cr(V) $\qquad$ $E^o \leqslant 0.65$ v.

(28) $\qquad$ Cr(VI) + 2e $\rightarrow$ Cr(IV) $\qquad$ $E^o < 1.13$ v.

(29) $\qquad$ Cr(V) + e $\rightarrow$ Cr(IV) $\qquad$ $E^o < 1.61$ v.
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 1.34$ v. (14)

(30) $\qquad$ Cr(V) + 2e $\rightarrow$ Cr(III) $\qquad$ $E^o > 1.67$ v.

(31) $\qquad$ Cr(IV) + e $\rightarrow$ Cr(III) $\qquad$ $E^o \geqslant 1.73$ v.
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad = 2.10$ v. (14)
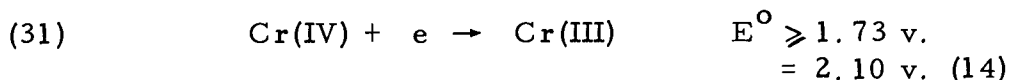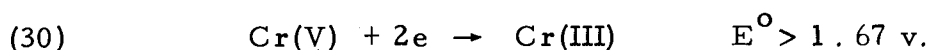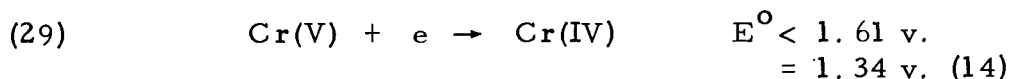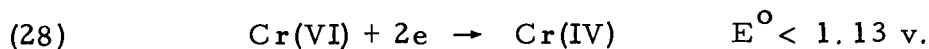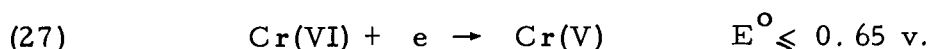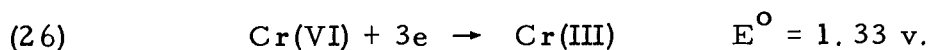
The second E^o values given for Equations (29) and (31) have been

reported as estimated values by Csanyi (14). Since the original

article is not available at this time, nothing can be stated about these

values and how they were obtained. These values are in accord with

the above estimated values since only lower or higher limits can be set.

Previous Studies of the Chromate-Iodide Reaction

The induced oxidation of iodide ion by the intermediate chromium(V) has been studied in many systems (7, 18, 24, 46). However, the reaction of iodide with chromium(VI) itself has been largely neglected. A detailed study of this reaction may, in fact, lead to a better understanding of the general mechanisms that are proposed and may elucidate the role the iodide ion plays in an induced reaction.

The chromium(VI)-iodide reaction was studied kinetically in 1903 by DeLurry (18, 19). He used the dichromate ion as the source for the chromium(VI) species and found that the rate of reaction was approximately first order in this ion. He did not maintain a constant ionic strength so his kinetic study did not yield much information. It did, however, suggest that the iodide dependence contained two terms, $k_a[I^-] + k_b[I^-]^2$. DeLurry found that the reaction rate was approximately second order in acid dependence; however, he was using H_2SO_4 in the acid region where the HSO_4^- dissociation cannot be neglected.

Taylor and Beard (6) in 1929 reported a more complete study of this system and they did keep the ionic strength constant at 1.50 M by using NaCl. They found an acid dependence as well as an iodide

ion dependence for the reaction. The rate law was given as:

$$(32) \qquad \text{Rate} = [HCrO_4^-] \left\{ k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2 \right\}$$

The hydrogen ion range was 1.81 to 4.54×10^{-2} M, and the iodide

ion range was 0.70 to 2.84×10^{-2} M. The chromate concentration

was 2.02×10^{-4} M. Only four points were obtained for the acid

dependence and four points for the iodide ion dependence. While

these points did indicate the above rate law, a more complete study

to confirm this rate law was definitely needed. Their study was made

by quenching samples from the reaction solution with acetate ion and

by titrating the iodine produced with thiosulfate.

In the 1950's a study was made that suggested chloride ion in

a chromate solution might influence the reaction. The system of

chromate, chloride, and hydrogen ions was studied by Haight et al.

(30). He found that there was a reaction between Cl^- and the chromate

ion:

$$(33) \qquad H^+ + HCrO_4^- + Cl^- \rightleftharpoons ClCrO_3^- + H_2O \qquad K = 11 \ M^{-2}$$
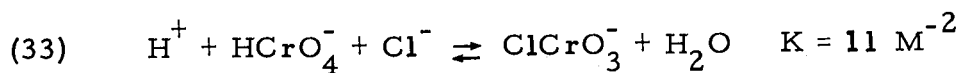
The value measured by Haight was $K = 17 \ M^{-2}$, but a later study

by Tong and Johnson (60) gave $K = 11 \ M^{-2}$. The latter value will be

used. Tong has shown that the value reported by Haight was based

on the false assumption of complete conversion to $ClCrO_3^-$ at 1 M HCl.

The addition of chloride ion could affect the chromate reaction by

producing a species, $ClCrO_3^-$, that would be either more or less

reactive than the $HCrO_4^-$. Bromide similarly could form a complex,

$BrCrO_3^-$. If the species, $ClCrO_3^-$ and $BrCrO_3^-$, do affect the rate of

chromate-iodide reaction, the magnitude of the change may be

related to the ability of the halogen to form the complex. Therefore,

the relative reactivity of the halogens toward the central chromium

could be studied. The high Cl^- concentration in the Beard and Taylor

study (6) would yield a solution that contained 33% of the $\Sigma[Cr(VI)]$

as the $ClCrO_3^-$ anion rather than the $HCrO_4^-$. This could have had a

great influence upon the kinetics observed.

Before the current work was completed, Howlett (36) published

a paper on the chromium(VI)-iodide reaction. He studied it kinetically

as an initial rate and used a titration method to follow the rate of

reaction. The dependencies of the iodide ion, hydrogen ion, and

chromate ion were determined by observing the initial rate of

reaction at various concentrations of all three ions. The various con-

centration ranges were:

$$[H^+] \qquad 0.40 \text{ to } 4.95 \times 10^{-2} \text{ M}$$

$$[I^-] \qquad 1.00 \text{ to } 4.00 \times 10^{-2} \text{ M}$$

$$[Cr_2O_7^{2-}] \qquad 1.98 \text{ to } 13.97 \times 10^{-3} \text{ M}$$

The rate law reported by Howlett was:

(34) $$\text{Initial Rate} = k[H^+]^2[I^-]^2[HCrO_4^-]$$

An interesting observation made in the study was that iodine retarded

the reaction. The chromate concentration in Howlett's work was much

higher than in either Beard and Taylor's (6) work, 2×10^{-4} M, or in the current study, 2×10^{-5} M. Therefore, the concentration of iodine that produces this retardation is much higher than that of any other study of the system.

For comparison purposes the article by Howlett does not contain much data except for one table of measured rates at the various concentrations of reactants. No initial rate plots, from which the rates were obtained, are shown. In a later plot of $d(I^-)/dt$ versus time, the plots appear to have a continuous curve. No unique tangent line seems to be available at the initial rate point. Therefore, the accuracy in obtaining the initial rates is not available in the article. It was also mentioned that slow runs in which the oxygen-iodide reaction could interfere were disregarded since those rates were always too high compared with the others. No attempt was made to remove the oxygen from the solutions. The increase in rate might have been due to another term of the type $k_1 [H^+] [I^-]$ in the rate law rather than having been due entirely to the oxygen-iodide reaction. Howlett also used the K_1 for chromic acid, Equation (1), that Neuss and Rieman (50) measured. As discussed previously, this K_1 value does not appear to be correct. The chromic acid concentration calculated for the kinetic runs in Howlett's work is therefore too large. The acid concentration in his study is low enough so that this correction does not affect the results very much. If his data is recalculated

using the K_1 = 4.16 M (59) the initial rate constant at 25° would be

lowered to $6.5 \times 10^4 \ M^{-4} \ sec^{-1}$ from $7.52 \times 10^4 \ M^{-4} \ sec^{-1}$.

Recent Studies Involving Other Inorganic Reducing Agents

In the last ten years chromium(VI) reactions with inorganic

reducing agents have been studied with renewed interest. The work

by Espenson and King (24, 25) has shown a mechanism for one elec-

tron transfer agents. The $Cr(VI)$-$V(IV)$ mechanism has been dis-

cussed earlier, Equations (17) to (19). Espenson and King's (25)

study of the $Cr(VI)$-$Fe(II)$ reaction gave a similar result.

(35) $Cr(VI) + Fe(II) \rightleftharpoons Cr(V) + Fe(III)$ equil.

(36) $Cr(V) + Fe(II) \rightarrow Cr(IV) + Fe(III)$ r.d.s.

(37) $Cr(IV) + Fe(II) \rightarrow Cr(III) + Fe(III)$ fast
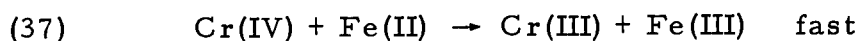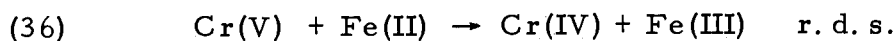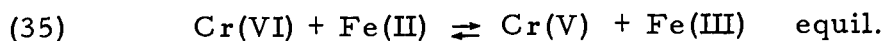
The rate laws for both of these reactions are given in Table 1. The

induced reactions of iodide in both the $V(IV)$ and $Fe(II)$ systems can

be explained by a rapid reduction of $Cr(V)$ to $Cr(III)$ by the iodide ion.

In these two studies by Espenson the slow step of the reaction

appears to be the conversion of $Cr(V)$ to $Cr(IV)$. In the reverse

reaction, oxidation of $Cr(III)$ to $Cr(VI)$, Tong and King (61) in a kinetic

study of the $Cr(III)$-$Ce(IV)$-system came to the same conclusion. In

this case the slow step was the conversion of $Cr(IV)$ to $Cr(V)$, and it

was suggested that a coordination change took place in this step. Tong

and King (61) cited evidence for this assumption. The $Cr(IV)$ and

Table 1. Summary of Rate Laws Proposed for Redox Reactions
Involving Chromic Acid and Inorganic Reducing Agents.

Reactant	Reference	Rate Law
VO^{+2}	(24)	$\dfrac{[VO^{+2}]^2}{[VO_2^+]}\left\{ k[HCrO_4^-] + k'[H^+][HCrO_4^-]^2 \right\}$
Fe^{+2}	(25)	$\dfrac{[H^+]^3[Fe^{2+}]^2}{[Fe^{3+}]}\left\{ k_1[HCrO_4^-] + k_2[HCrO_4^-]^2 \right\}$
$H_2AsO_3^-$	(47)	$\dfrac{k[As(III)][Cr(VI)]}{1 + k'[As(III)]}$
HSO_3^-	(31)	$\dfrac{k[HCrO_4^-][HSO_3^-]^2[H^+]}{1 + k_c[HSO_3^-]}$
H_3PO_3	(52)	$\dfrac{k[Cr(VI)][H_3PO_3][H^+]}{1 + k_5[H_3PO_3]}$

Cr(III) both appear to have a coordination number of six whereas

Cr(VI) and Cr(V) both have a coordination number of four.

This type of mechanism appeared to be the normal one for a

reaction of Cr(VI) with a one electron reducing agent. However,

Espenson and King (25) found that if the Fe(II) ion is complexed to

form the non-labile tris-(1,10 phenanthroline)-iron(II) ion, the rate

law is changed. The slow step becomes the reduction of Cr(VI) to

Cr(V) instead of being the Cr(V) to Cr(IV) step. The difference in

the reactivity of hexaquoiron(II) ion and the non-labile iron(II) com-

plex must be in the coordination of the iron to the chromate ion. The

hexaquoiron(II) ion can form the complex Fe(II)-O-Cr(VI), and this

complex can be stable enough to exist until a second Fe(II) reacts with

it. The tris-(1,10 phenanthroline)-iron(II) ion cannot form this com-

plex with Cr(VI). The difference between the slow steps of the two

reactions was related to this ability of hexaquoiron(II) ion to form a

complex with the chromate anion.

Reducing agents that can lose two or more electrons have been

studied by Haight. Some of the systems which have been studied

involved the P(III) (52), S(IV) (31), and As(III) (47) species. The rate

laws, listed in Table 1, for these systems differ from the ones found

for one-electron reducing agents. The As(III) and P(III) reactions were

reported to have two electron transfers in the rate determining step,

and S(IV) was reported to have a three electron transfer step. In

these studies, the formation of a chromate complex has always been included, and a steady-state treatment for the complex has yielded the denominator term in the rate laws. The following reaction with As(III) is shown as an example of this type of mechanism.

$$(38) \qquad As(III) + HCrO_4^- \rightleftharpoons As(III) \cdot HCrO_4^-$$

$$(39) \qquad As(III) \cdot HCrO_4^- \rightarrow rate\ determining\ step$$
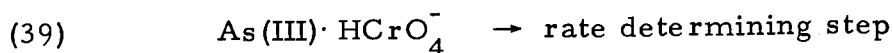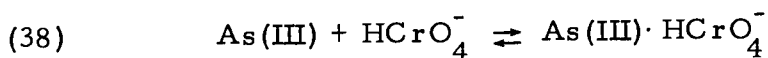
The first step is an equilibrium in which a Cr(VI)-As(III) complex is formed. The rate determining step is the reaction of this complex. The slow step is assumed to be the reduction of Cr(VI) to Cr(IV).

The complex formation has been studied in more detail by Haight (27). He used $H_2PO_4^-$ so that no oxidation-reduction process would mask the result. The formation of the chromate-$H_2PO_4^-$ complex was studied kinetically and found to be aided by general acid catalysis. Therefore, the postulation that chromate complexes are involved in reactions can be made with justification, and in fact it has been used in almost every reaction to explain the observed kinetics.

Summary

The iodide ion can be either a one or a two electron reducing agent. The chromate-iodide reaction could be related to either of these two types of reactions or maybe to both. A rate law with a denominator term in iodide would indicate the two electron process. The kinetic system can be made less complex if the concentrations of

acid and chromate are made so that only one form of Cr(VI) is present. In $[H^+]$ of less than 0.10 M and $[Cr(VI)]$ less than 1×10^{-4} M, the $HCrO_4^-$ is the only major chromate species present. The influence of Cl^- and Br^- on the reaction rate can be investigated to see if an order of reactivity for the halogens toward the chromate ion can be determined. Information about the mechanism after the rate determining step may be obtained by adding scavengers, such as Mn(II) ion, for the chromium intermediates.

EXPERIMENTAL

Reagents

The potassium iodide, potassium perchlorate, potassium nitrate, sodium nitrate, and potassium chromate were all B&A reagent grade chemicals. All the solid reagents were dried in an oven at 110° and were then stored in a vacuum desiccator over Drierite ($CaSO_4$). Since none of the reagents are hygroscopic, this treatment seemed adequate. The perchloric acid used was either Baker Analyzed 60 - 62% reagent grade or B&A 70% reagent grade. These two sources of acid did not produce any change in the measured rate of reaction.

The manganese(II) perchlorate was from G. Frederick Smith Chemical Co. The manganese(III) ion was generated in a 1 M $HClO_4$ solution by the method described by Diebler and Sutin (20). The manganese(II) perchlorate was dissolved in the 1 M $HClO_4$ to give a 0.1 M concentration of Mn(II) ion. Two platinum electrodes were used for the inert electrodes. A Heath EUW-17 transistor power supply was used, and the current was maintained at approximately 12 milliamperes for 150 seconds. This treatment produced a 8.4 X 10^{-5} M solution of Mn(III) ion as measured from its production of iodine in a KI solution.

Eastman White Label allylacetate was used without further purification. The benzaldehyde was Matheson, Coleman and Bell, chlorine-free grade. This benzaldehyde reacted with an aqueous solution of potassium iodide to produce iodine. To purify it further, the benzaldehyde was distilled from potassium iodide crystals, and the vapor was passed through a Vigreaux column. This distillation was carried out at a reduced pressure, approximately 27 torr, with a nitrogen capillary bleeder. The product was kept in a glass-stoppered flask filled with nitrogen. This flask was placed inside the nitrogen atmosphere box.

The hexaquochromium(III) perchlorate was prepared using a method similar to that described by Hougen, Schug, and King (34) and Espenson (23). B&A reagent Chromium Trioxide (0.11 moles) was dissolved in a 2.0 M $HClO_4$ solution (200 ml) and was reduced by a slight excess of formic acid, 88.5% reagent grade. The solution turned to the blue-violet color of the chromium(III) ion. To insure complete reaction the solution was heated at 50° - 60° for two hours. The solution was concentrated by using a rotary evacuator and was cooled to crystallize the $[Cr(H_2O)_6](ClO_4)_3$. The product was recrystallized from a 0.01 M solution of $HClO_4$ and was dried over P_2O_5. The product was deliquescent and contained some $HClO_4$ from the recrystallization. Hexaquochromium(III) perchlorate from G. Frederick Smith Co. was also used. In either case the

concentration of Cr(III) ion was determined by oxidizing it to the CrO_4^{2-}. For this oxidation the solution was made basic by adding NaOH until the green color of $Cr(OH)_4^-$ appeared. The oxidizing agent, H_2O_2, was added to convert $Cr(OH)_4^-$ to CrO_4^{2-}. Potassium salts were avoided since the resulting $KClO_4$ would precipitate. The concentration of CrO_4^{2-} was determined by the measurement of the absorbance of the solution at $\lambda = 375$ mμ ($\epsilon_{375} = 4820$ M^{-1} cm^{-1}) (33).

Instrumentation and Temperature Control

A Beckman DU spectrophotometer equipped with a tungsten lamp source was used to follow the reaction kinetics. The cell holder was thermostated using water cooled baffles which were placed next to the cell block holder. The water for these baffles was supplied by a constant temperature bath with a thermo-regulator for temperature control. A constant temperature of $\pm 0.02°$ could be maintained for several hours. The temperature control was, however, slightly dependent upon the ambient temperature. The cell temperature would be approximately $0.1°$ higher at an ambient temperature of $30°$ than at $25°$. The cell temperature maintained throughout the various seasons was $\pm 0.1°$.

The temperature inside the cell compartment was measured with a thermistor and a Wheatstone bridge. The thermistor was

calibrated in a constant temperature bath with a thermometer which had been standardized against a NBS standardized thermometer. A temperature curve of degrees versus the ohm reading of the bridge was made with five to six readings covering a one degree temperature range. A temperature curve, linear over the one degree range, was made for each temperature used in this study. The thermistor was placed inside the cell block holder where the reaction cell would be. The thermistor reading was taken as the resistance measurement on the Wheatstone bridge. The temperature in the cell block could then be determined $\pm 0.01°$ from the plots of temperature versus bridge reading.

The temperature control was started at least two hours before the beginning of the kinetic runs, and the tungsten lamp was also turned on at the same time. This procedure was necessary to have complete temperature equilibrium in the cell holder. Likewise, the reference cell and empty cells were placed in the compartment at this time. Reaction mixtures were brought to the desired temperature in a constant temperature bath which was set at the same temperature as the cell compartment $\pm 0.1°$.

Some kinetic runs were rapid enough ($t_{\frac{1}{2}} < 600$ sec.) that measurements on the DU spectrophotometer were difficult to take manually. The DU was equipped with a Beckman energy-recording adapter (ERA). The output of the photomultiplier tube was displayed

directly on a strip-chart recorder. This signal was recorded as the percent transmittance of the sample. The dark current and 100 percent transmittance settings of the DU had to be made on a water reference cell before the reaction cell was placed in the light beam. These limits were assumed not to change during the reaction and were rechecked at the end of the kinetic run. This assumption was usually good for under 900 sec., but beyond that time period the limits would sometimes change over one percent from either the zero or the 100 percent transmittance limit. Therefore, manual measurements were used for reactions with half-lives predicted to be over 450 seconds.

The strip-chart recorders used with the ERA were the Heath Kit EUW 20A recorder, equipped with a variable chart speed drive, EUA-20-26, and a Varian Recorder, G-14. The Varian recorder had interchangeable motors to vary its chart speed. The kinetic data was not dependent upon recorder type. The recorders were turned on for at least two hours before each kinetic run so that they could attain electronic equilibrium.

Reaction Conditions

The kinetic runs were prepared in approximately the same way each time. The dissolved oxygen content of the solution was of major importance since the concurrent reaction between oxygen and

iodide in an acid solution had to be kept at a minimum. The procedure for treating the solution to remove most of the oxygen will be discussed in the next section.

Double-distilled water was used in preparing the solutions. The first distillation was from a basic permanganate solution, and the second distillation was made to remove all traces of the permanganate ion. The reactant, potassium chromate (K_2CrO_4), was weighed, placed in a one liter volumetric flask, and diluted to the mark with the double-distilled water. A ten ml aliquot was taken from this solution and was placed in a fifty ml flask. A stock solution of $HClO_4$ was made and was standardized against $1/10$ N CO_2-free Hellige Certified Reagent or Acculute NaOH. The measured volume of acid solution was placed in the same fifty ml flask with the chromate solution. Potassium iodide was weighed directly into a second twenty-five or fifty ml volumetric flask. To bring the ionic strength to 0.130 M, potassium perchlorate was used in all runs except in the ionic strength study and in the vac-line runs. In those runs potassium nitrate was used. Since $KClO_4$ has a low solubility (0.119 M) (45) at 20°, it was normally weighed directly into both the reaction mixture flasks. At high iodide or hydrogen ion concentrations very little potassium perchlorate was needed, and then it was weighed directly into only one of the reactant flasks.

The two reaction flasks were placed in a constant temperature

bath to come to the reaction temperature. In runs with half-lives of over ten minutes a ten ml portion of one reactant was transferred by means of a pipette to a glass-stoppered flask filled with nitrogen. This flask was also placed in the temperature bath. The reaction was initiated when a ten ml pipette of the second mixture was transferred to the glass-stoppered flask. The time zero was taken to be the moment the second mixture reached the midpoint in the pipette cavity. The solution was then mixed by shaking the flask. After it was mixed, the solution was transferred to a 1.0 cm. spectrophotometer cell. The mixing time was normally less than thirty seconds, and the first absorbance reading was recorded at approximately seventy seconds.

For reactions with half-lives of less than ten minutes the preceding method of initiating the reaction was too long compared to the reaction rates. In these runs, ten ml. pipettes were used to transfer the reaction mixtures to two separate glass-stoppered flasks. The reaction was initiated and the solutions were mixed by pouring the solutions back and forth between the two flasks. Using this technique mixing time was ten seconds, and the first absorbance reading could be made in forty seconds if it was taken manually. Using a strip-chart recorder and the ERA, the first absorbance reading could be made in thirty seconds.

In kinetic runs in which other chemicals were added in addition to the main reactants, the procedure was essentially the same. Only

in the allylacetate experiment did the reaction appear to depend on the flask in which the chemicals were added. The allylacetate had to be added to the KI solution in order to produce the correct amount of triiodide in the chromate-iodide reaction. The kinetic runs with added benzaldehyde did not differ whether the benzaldehyde was added to the initial KI or $HCrO_4^-$ solution. Since there was an initial reaction between an impurity in the benzaldehyde and KI, the benzaldehyde was added to the starting KI solution to insure complete reaction of this impurity. In the other cases tested the order of the addition of chemicals did not seem to matter. Normally, the additional chemicals were added to the starting KI solution. The solid reagents were weighed directly into one of the volumetric flasks. The allylacetate or benzaldehyde was first diluted to the desired concentration in a separate volumetric flask, and then a portion of this solution was measured into the volumetric flask of the reactant.

After the solutions were mixed and transferred to the 1.0 cm. cell, the reaction was monitored in the DU Spectrophotometer. The triiodide ion which was produced in the reaction had the highest extinction coefficient of any reactant or product in the region of 350 mμ. The triiodide ion had an absorbance of 26,400 M^{-1} cm^{-1} at 353 mμ (3). Therefore, the majority of the runs were followed at the 353 mμ wavelength. It can be assumed that this wavelength was used for all runs unless they are otherwise labeled.

The rate of reaction did not seem to be dependent upon the wave

length used for measurement. Table 3 contains the k_{obs} for runs

with initial $[HCrO_4^-]$ = 1.50 $\times 10^{-5}$ M at λ = 287.5, 353, and 410 mμ.

The light beam was also tested to see if it had any influence upon

the reaction. Two identical kinetic samples were made, and one

was placed in position four, farthest from the light beam; this sample

was measured infrequently. The second sample was always positioned

in the light beam, and a maximum slit width, 2.0 mm., was used.

No difference could be detected between the two kinetic runs, and

points from each run fell on the same curve.

The DU Spectrophotometer is capable of holding four 1.0 cm.

cells; therefore, more than one reaction can be followed at a time.

In most cases one cell was used for the reference sample which in

this study was distilled water. A blank which contained all the

reactant species except the chromate ion was also made. This blank

was made up at the same time the regular run was being prepared,

and the same water and oxygen precautions were used. The normal

iodide-acid-oxygen reaction could be corrected for in the kinetic

run by monitoring this blank. In most cases the oxygen-iodide

reaction was too slow to make corrections necessary in the reaction

rate. The corrected slope obtained was within a percent of an

uncorrected slope. The end-point value at infinity reaction time,

A_∞, was obtained by subtracting the rate of change in the blank cell

from the rate of change in the reaction cell. Since the blank did not always change at exactly the same rate as the reaction cell, this procedure sometimes gave obviously erroneous A_∞ values. In cases in which this correction was definitely in error the A_∞ reading was obtained by following the change in A_∞ with time after 10 $t_{\frac{1}{2}}$ were past, and these changes were used to extrapolate back to the correct A_∞. The A_∞ values were normally 0.01 - 0.02 from the theoretical value. To make a 5% error in the rate, a value of 0.025 or higher would have to be added to the A_∞ value. This process was therefore believed to be adequate, and in the majority of runs this correction was only a minor one, ±0.01 absorbance units. The N_2-box and vac-line kinetic runs were the only ones in which the blank procedure was not necessary.

Some problems with A_∞ values were encountered when the DU cells were completely filled. The solution around the stopper seemed to evaporate, and a high concentration of I_3^- developed. If the solution was in contact with the cap, the A_∞ values changed rapidly with time. This problem can be avoided by keeping the solution off the stopper joint, and by not completely filling the cell.

Removal of Oxygen

As mentioned earlier, the oxygen content of the solution was a major consideration in this kinetic study. The reaction between iodide

and oxygen in the acid solution could result in faulty kinetic data.

Also, the absorbance at time infinity from the chromate reaction

could not be obtained with great accuracy because of the increase of

triiodide from this oxygen reaction. The following procedures were

used to ascertain the influence of oxygen on the reaction under study.

The majority of kinetic runs were made under what will be

labeled N_2-flush conditions. The kinetic rate law was obtained from

experiments under this condition and is to be considered the type of

run made unless otherwise stated. In this condition the double-dis-

tilled water was boiled briefly, and a gas dispersion tube was used

to disperse a stream of prepurified nitrogen through the water while

it was cooled. The solutions were all diluted with this water, and

nitrogen was kept over the solutions as much as possible. The acid

and chromate stock solutions were made up this same way. Since it

was convenient to make these two solutions beforehand and to keep

them for a series of runs, the nitrogen atmosphere had to be main-

tained over the solutions. A sealed bottle with two glass tubing out-

lets was used for this purpose. Tygon tubing was attached to one of

the glass tubes, and a clamp was placed on it. The other glass tube

had a nitrogen-filled balloon connected to it. The balloon adjusted

inside pressure whenever a portion of the acid or chromate was taken

from the bottle through the Tygon tubing. These stock solutions were

good for one week before the oxygen content became appreciable as

revealed by an increase in the absorbance of the blanks containing

iodide and hydrogen ions.

For comparison, a variety of other oxygen content conditions

were also tried. The kinetic runs labeled N_2-box refer to the solu-

tions that were made up entirely inside an inert-atmosphere box

with nitrogen as the flush gas. The stock solution of acid was made

by placing the amount of acid needed in a volumetric flask, and by

diluting it with water inside the inert-atmosphere box. All solids

were weighed into the flasks and then placed inside the box. A

nitrogen gas outlet tube inside the box was used to flush out all flasks

placed inside. The water used inside the box was the double-

distilled water. This water was boiled outside the box, and placed

inside the entry-box where it was cooled under a stream of nitrogen.

The water was then moved inside the main box. Each entry into the

inert atmosphere box was made by placing the article in the entry

box which was then purged with nitrogen for one hour. Likewise, a

twenty-four hour nitrogen flow was continuous into the inert-atmos-

phere box, and a positive pressure was maintained inside the box

between runs.

The simplest oxygen condition is the one used for kinetic runs

labeled air. These experiments were carried out in the air mixture

of nitrogen and oxygen with no precautions taken. The experiments

labeled O_2-flush are similar to the N_2-flush experiments, except that

oxygen was used as the cooling gas. Likewise, the solutions were kept under an oxygen atmosphere.

The final technique used for oxygen control is labeled vac-line, and refers to the kinetic experiments using the vacuum line. In this process a degassing cell (40) pictured in Figure 1 was used to contain the reactants. One ml of the KI solution was placed in compartment A and three ml. of the chromate solution were placed in compartment B. The solutions were frozen with a dry ice--acetone bath, -80°, and the stopcock was opened to the vacuum line. After the degassing cell was evacuated, the vacuum pump was isolated from the vacuum line, and approximately 730 torr of pre-purified nitrogen was allowed to enter the cell. The stopcock was again closed, and the reactants were thawed. After they were thawed, the solutions were again frozen and the cycle repeated. Experiments in which this cycle was repeated twice indicated that most of the dissolved oxygen was eliminated; the A_{∞} values did not change over a period of several hours. However, in all kinetic runs the cycle was repeated three times.

If the water vapor over the -80° solid is assumed to be an ideal gas, and it is further assumed that it comes to equilibrium in a one liter volume, the percent of water lost in each evacuation cycle is approximately 1×10^{-5}%. This amount is negligible in this study. The saturation of water vapor in the N_2 gas during each thawing may be a more important problem. Most of this vapor was regained when

the solutions were refrozen. Therefore, the concentrations of the solutions were presumed to be unchanged during this process, and the kinetic data confirmed this belief.

After the freeze-pump-thaw cycle was completed, the degassing cell was filled with approximately 730 torr pressure of prepurified N_2 and was removed from the vacuum line. It was placed in the constant temperature bath to bring it to reaction temperature. To initiate the reaction the cell was tipped sideways to bring the liquids into contact, and then the cell was thoroughly shaken. The DU cell was filled by shaking the liquid down the side arm into the cell. The cell was then removed from the side arm and immediately stoppered with a teflon cell stopper. The degassing-cell side arm had a cut $\mathbb{T}$ 10/18 joint which fits the opening in a Photo Volt cell.
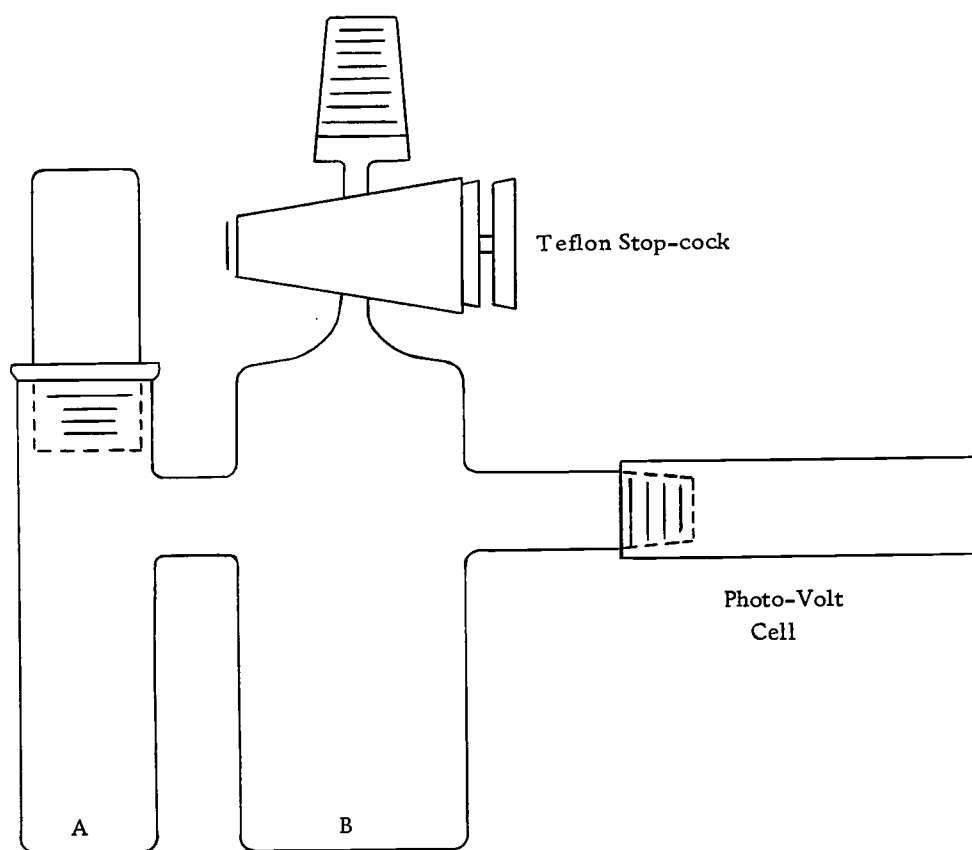
Figure 1. Degassing Cell Used on the Vacuum Line.

STOICHIOMETRY

The stoichiometry of the reaction

(40) $\quad 2HCrO_4^- + 9I^- + 14H^+ + 4H_2O \rightarrow 2Cr(H_2O)_6^{3+} + 3I_3^-$
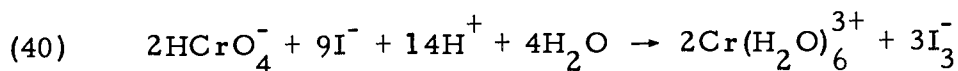
has been confirmed except for the iodide ion. In the study by Howlett (36), this remaining stoichiometry was confirmed under conditions in which the iodide ion concentration was comparable to the chromate ion concentration. In the following experiments the different species were determined relative to the number of millimoles of K_2CrO_4 which were dissolved in the acidic solutions to give $HCrO_4^-$.

Triiodide Ion

The amount of iodine produced by a known quantity of $HCrO_4^-$ was determined spectrophotometrically. Since dissolved oxygen in solution can also produce iodine, the oxygen content of the solution had to be kept at a minimum. The kinetic runs made in the nitrogen-atmosphere box can be used for this stoichiometric measurement. By using the absorption of triiodide ion at 353 mμ, ϵ = 26,400 M^{-1} cm^{-1}, the amount of triiodide ion produced from the starting chromate concentration can be calculated.

The iodine produced has been written in the form of the tri-iodide ion, and this formulation is proper for the major species

produced in the kinetic runs. However, for experiments in which the

iodide concentration is smaller than 0.04 M, three percent or more

of the form I_2 is produced. Therefore, the notation I_3^- should be

replaced by $\Sigma[I_2]$, since $\Sigma[I_2] = [I_3^-] + [I_2]$. The equilibrium

constant for the association

(41) $$I_2 + I^- \rightleftharpoons I_3^- \qquad K = 870 \text{ M}$$
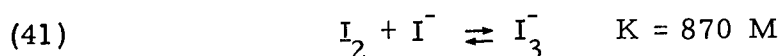
has been measured by Katzin and Gebert (38). Their value has been

chosen (see introduction on iodine species) since it was measured

at 20° in a solution containing 0.01 M $HClO_4$ and at 0.10 M ionic

strength. These conditions are very close to the ones encountered

in this work. Using this value the I_2 produced in the reaction was

calculated from the final absorbance of the I_3^-: $\Sigma[I_2] / [CrO_4^{2-}]_o$

observed = 1.50; $\Sigma[I_2] / [CrO_4^{2-}]_o$ theoretical = 1.50.

Hydrogen Ion

The stoichiometry of the hydrogen ion was determined by titra-

tion with a base after the reaction had gone to completion. Since

iodine was also produced in the reaction, it had to be removed with

thiosulfate before the base titration. This titration would not affect

the hydrogen ion content since the reaction

(42) $$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$
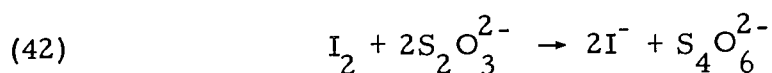
does not involve acid in its stoichiometry. The iodine must be

removed since the reaction

(43) $$I_2 + OH^- \rightarrow IOH + I^-$$
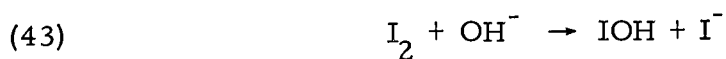
proceeds in a basic solution, and the acid titration would have to be

corrected for this iodine reaction.

The initial chromate ion concentration had to be increased from

the normal kinetic concentration, 2×10^{-5} M, to 3×10^{-3} M in order

to have a measurable change in the hydrogen ion concentration. The

initial hydrogen ion concentration was .0458 M. The results were:

Mmoles $CrO_4^{2-} \times 10^1$	Mmoles $HClO_4 \times 10^1$	Ratio $[H^+]/[CrO_4^=]$
1.524	7.622	5.002
1.447	7.322	5.060
0.788	3.903	4.924
	average	5.00

The reaction stoichiometry requires eight protons per chromate ion

instead of five as shown above. During the titration a precipitate

formed, and this species could only be $Cr(OH)_3$. The missing three

hydrogens can be accounted for in the precipitation of the $Cr(III)$

reaction product.

(44) $$Cr(H_2O)_6^{+3} + 3OH^- \rightarrow Cr(OH)_3 \times H_2O$$
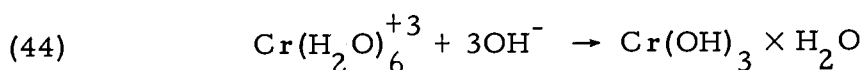
In order to verify the complete precipitation of $Cr(III)$ and to

show that it was not further redissolving to give $Cr(OH)_4^-$,

hexaquochromium(III) perchlorate was dissolved in water, 2.08×10^{-2} M, and titrated to the phenolphthalein end-point. The amount of base required to precipitate the Cr(III) was then calculated and the number of OH^- per Cr(III) could be determined.

Mmoles Cr(III)	Mmoles OH^-	Ratio OH^-/Cr(III)
1.04	3.189	3.07
1.04	3.214	3.09
1.04	3.204	3.08
	average	3.08

The results indicate that $Cr(OH)_3$ is completely precipitated with the desired stoichiometry of three hydroxides. The slight difference between the theoretical 3.00 and the observed 3.08 might be due to the $HClO_4$ which stays with the $[Cr(H_2O)_6](ClO_4)_3$ during the recrystallization step. Another possibility is that $Cr(OH)_4^-$ is beginning to form. This difference is considered small enough to be neglected for this stoichiometry measurement.

The stoichiometry of the hydrogen ion must then be calculated by taking into account the acidic behavior of the Cr(III) product. Therefore, the total number of hydrogen ions used during the reaction is given by adding the results of the above two tables. The result is:

$[H^+]/[CrO_4^{2-}]$ observed = 8.08; $[H^+]/[CrO_4^{2-}]$ theoretical = 8.00.

Chromium(III) Product

The most reasonable products that could appear from the reaction are $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5I^{2+}$, and the dimer $[(H_2O)_5CrOCr(H_2O)_5]^{4+}$. The dimer is a doubtful major species in the kinetic runs since the total chromium content is only 2×10^{-5} M. The stoichiometry and identity of the chromium(III) species were determined by two different methods.

The first method of identification was a spectral analysis of the products after the iodine was titrated with thiosulfate. No interaction between the chromium product and the thiosulfate or tetrathionate was assumed. In this perchloric acid system the $Cr(H_2O)_6^{3+}$ cation was believed to be the end product. A solution of 2.24×10^{-2} M $[Cr(H_2O)_6](ClO_4)_3$ was prepared so that the Cr(III) reaction product spectrum could be compared to a known spectrum. The initial concentrations for this study were $HCrO_4^- = 1.279 \times 10^{-2}$ M, $KI = 1.8$ M , and $HClO_4 = 0.5$ M. The $HCrO_4^-$ concentration was 1,000 times higher than it was in a normal kinetic run, but the higher concentration had to be used in order to see the final Cr(III) spectrum. After one hour, a ten milliliter aliquot was taken from the reaction flask. The triiodide ion was titrated with 3.11 ml. of 0.123 M thiosulfate. Because of this addition of thiosulfate, a new concentration of chromium(III) had to be calculated, 9.755×10^{-3} M.

The chromium(III) product from this experiment gave two absorption peaks with the following absorbance coefficients, based upon the initial $HCrO_4^-$ concentration: $\epsilon_{408} = 16.1$; $\epsilon_{575} = 13.6$ M^{-1} cm^{-1}. The known solution of hexaquochromium(III) perchlorate gave absorbance coefficients of $\epsilon_{408} = 16.0$ and $\epsilon_{575} = 13.6$ M^{-1} cm^{-1} (22, 51). Therefore, the final product of the reaction appears to be $Cr(H_2O)_6^{3+}$. The spectrum scans were made on a Beckman DK-2 and the determination of peaks and the absorbance measurements were made on the Beckman DU.

The above method gave the final product after the reaction had been allowed to stand for one to two hours. It did not separate the individual species of the reaction product. Many species absorb in the same general wavelength region, as summarized in Table 2. If the absorbances of the monomer, $Cr(H_2O)_6^{3+}$, and the dimer are added together, they could give the appearance of being in a single form such as the monomer. The $Cr(H_2O)_5I^{2+}$ does have a spectrum distinct from the other two forms; however, it aquates to the hexaquochromium(III) ion. The half-life of this aquation is approximately one hour under the above conditions of 0.5 M $HClO_4$ (58). Therefore, its presence could have been missed. A different means of product identification was desired although the ultimate species produced appeared to be the $Cr(H_2O)_6^{3+}$.

Table 2. Summary of the Absorbances of Possible
Cr(III) Products.

Species	Peaks mμ	Molar Absorbance Coefficients, ϵ, M^{-1} cm^{-1}	
$Cr(H_2O)_6^{3+}$	408	16.0	(22, 51)
	575	13.6	
dimer	410	22	(1)
	580	16	
$Cr(H_2O)_5I^{2+}$	260	5740	(58)
	474	32.6	
	650	36.1	

An ion exchange column was used for the second method of

chromium product identification. This method had the desirable

feature of separating the different charged species so that the

spectra of the individual products could be obtained instead of a

composite spectrum. The main species which was sought in this

experiment was the $Cr(H_2O)_5I^{2+}$ since it could give a clue to the

mechanism of the reaction.

Using the above spectral method there was no indication of the

iodochromium(III) ion, but major aquation of this ion could have taken

place. Therefore, this experiment was designed for low tempera-

tures, $0°$, and a short time period. The initial concentrations of

reactants were $HCrO_4^- = 5.12 \times 10^{-3}$ M, KI = 4.5 M, and

$HClO_4 = 0.100$ M with the total volume equal to 50 ml. After four

minutes of reaction time, the flask was placed in an ice-water bath,

and then a sample was placed on the ion-exchange column.

The ion exchange column resin was Dowex--50 W4 50-100 mesh.

The resin, which was washed with 1 M $HClO_4$ in a batch process,

was used in the hydrogen ion form. A column size of approximately

47.4 meq. of exchange capacity, 25 ml. of wet resin, was used.

The number of milliequivalents of exchange capacity in the reaction

solution was always less than the amount in the column. The column

consisted of a condenser with a rubber tube for the outlet and a

screw clamp for the regulator. Ice water was circulated through

the condenser jacket by means of a small water pump in an ice-water

bath. When using this process all exchange work could be done at 0°.

After the sample was placed on the exchange column, the

triiodide ion had to be washed through the column. The iodine or

triiodide ion did not appear to react with the column material; how-

ever, it became adsorbed on the column. The wash solution was

0.1 M $HClO_4$, and it had to be run through the column for one hour,

at the rate of 6 ml/min, to remove most of the iodine. There was

still a yellow coloration due to iodine in the wash solution after this

period. Further washing was discontinued to keep the time element

as short as possible. After the major portion of I_2 was washed

through, the eluant was changed to a 1.0 M $HClO_4$ solution, flow

rate of 4 ml/min, in order to elute any plus two charged species.

After the column was washed, a blue-violet band tinged with green was present at the top of the column. The 1.0 M $HClO_4$ eluant separated this band into two visible ones; a large blue-violet band appeared below a small green band. The blue-violet band moved slowly down the column at the same rate as a known $Cr(H_2O)_6^{3+}$ sample. The band was assumed to be the $Cr(H_2O)_6^{3+}$. The green band stayed at the top of the column and did not appear to move. According to Swaddle and King (58), this technique should separate the $Cr(H_2O)_5I^{2+}$ from the $Cr(H_2O)_6^{3+}$, and a green band of the former should appear below the blue-violet band. There was no green band observed for the iodochromium ion.

The eluant from the column in front of the blue-violet band was collected in four portions of 10 ml. each. These were analyzed for any $Cr(H_2O)_5I^{2+}$ that would come off before the $Cr(H_2O)_6^{3+}$. The faint yellow color of iodine was removed using thiosulfate, and each solution was monitored at 260 mμ. The $Cr(H_2O)_5I^{2+}$ had a maximum absorbance of 5,740 M^{-1} cm^{-1} at this wave length, while $Cr(H_2O)_6^{3+}$ had only a weak absorbance of about 5 M^{-1} cm^{-1} (58). The data obtained is summarized below.

Portion #	Absorbance	Mmole $Cr(H_2O)_5I^{2+}$
1	0.224	9.8
2	0.090	0.4
3	0.060	0.3
4	0.046	0.2

If the absorbance is assumed to be due entirely to the iodochromium-
(III) ion, then the number of millimoles of this ion in each portion is
given in the last column. The absorbance is probably not due
entirely to the iodochromium ion since thiosulfate was used to remove
the iodine. The tetrathionate that was formed also has an absorbance
at this wave length, ϵ_{260} = 560 M^{-1} cm^{-1} (3) and could account for
most of the absorbance found in the fourth portion.

After the four 10 ml. portions were collected, the dark-violet
band was eluted from the column with 1.0 M $HClO_4$ and was col-
lected in two 25 ml. portions. This band gave absorbance peaks at
480 mμ and 575 mμ with the required absorbance for the $Cr(H_2O)_6^{3+}$
cation, ϵ_{408} = 16.0 M^{-1} cm^{-1}, and ϵ_{575} = 13.6 M^{-1} cm^{-1}. The
Cr(III) ion concentration was determined by the oxidation with
alkaline H_2O_2 as described previously, and it accounted for 85%
of the total chromium.

These results again show the hexaquochromium(III) ion to be
the major product. The total amount of $Cr(H_2O)_5I^{2+}$ that could be
present, assuming no other absorbing species at 260 mμ, is 0.5% of
the total chromium. The $Cr(H_2O)_5I^{2+}$ is therefore eliminated as a
species that must be regarded in the reaction mechanism. The
remaining 15% of the chromium was either left on the column as the
hexaquochromium(III) ion or was in the green band which could not
be eluted.

Since the green band could not be eluted, its charge must be higher than plus three. The only reasonable species is a dimer of chromium(III) and it probably has a plus four charge, $[(H_2O)_5CrOCr(H_2O)_5]^{4+}$. This species could only account for 15% of the product, however, the initial chromate concentration in this experiment was 100 times greater than that used in the kinetic runs. The dimer could result from the interaction

(45) $$Cr(III) + Cr(VI) \rightleftharpoons Cr(III)-O-Cr(VI)$$
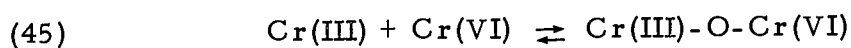
reported by King (41). The $Cr(III)-Cr(VI)$ species is reduced with iodide ion to the $Cr(III)-Cr(III)$ dimer. In this more concentrated chromate solution, the dimer is much more important. In the normal kinetic run this dimer is probably present in less than a percent of the total chromium. Unfortunately, the equilibrium constant for the above reaction is unknown, and quantitative results cannot be given.

RESULTS

Kinetics

Pseudo-First Order Kinetics

The chromate ion is involved in a variety of equilibria in an aqueous acid solution. These equilibria were discussed in the introduction under "The Chromate Equilibria". The hydrogen ion concentration in this study varied from 0.0095 to 0.1036 M, and the total chromium(VI) concentration varied from 0.35 to 4.5×10^{-5} M. The main equilibria that must be considered are:

$$(46) \qquad 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} \qquad K_{22} = 98 \quad M^{-1}$$

$$(47) \qquad H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \quad K_1 = 4.1 \ M$$
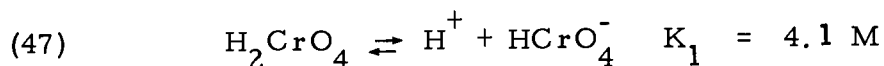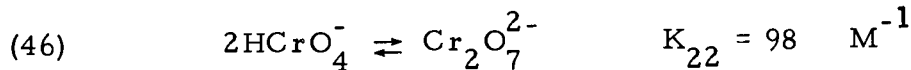
The values for these equations were discussed in the introduction. Under the conditions studied here, the dimer, $Cr_2O_7^{2-}$, accounts for only 0.9% of the $\Sigma[Cr(VI)]$ in the run with the highest concentration of $HCrO_4^-$. This species can therefore be completely neglected. The chromic acid, H_2CrO_4, accounts for 2.4% of the $\Sigma[Cr(VI)]$ in the 0.1036 M $HClO_4$ run and is on the borderline of becoming important. Considering the disagreement as to the exact value of K_1 this correction was not made on these higher acid runs. The error in picking the correct value of K_1 might give a larger error

than the 2% correction it would produce in the data. The only species

in the reaction solution is assumed to be the $HCrO_4^-$ in this kinetic

study.

The initial concentrations of iodide and hydrogen ions were

always large compared to the concentration of the $HCrO_4^-$. The

minimum ratios were $[I^-]/[HCrO_4^-]_o$ = 250 and $[H^+]/[HCrO_4^-]_o$ =

480. The assumption was then made that the only reactant that

changed with time was the $HCrO_4^-$. The final concentrations of the

iodide and hydrogen ions did not differ significantly from their initial

concentrations. The following equation gives the mathematical

expression for the change in the $[HCrO_4^-]$ with respect to time.

(48) $$\frac{-d[HCrO_4^-]}{dt} = k_{obs}[HCrO_4^-]^n$$

in which n is reaction order of the chromate species and k_{obs} is

the pseudo-order rate constant. The absorbance of triiodide ion

was the quantity measured in the kinetic runs. The k_{obs} contains

the dependence of the reaction on the concentrations of the iodide and

hydrogen ions. Since they did not change in an individual kinetic run,

the iodide and hydrogen ions are combined into the pseudo-order

constant.

The reaction was assumed to be first order in $HCrO_4^-$. The

integrated rate expression from Equation (48) becomes

(49) $\ln([HCrO_4^-]_t/[HCrO_4^-]_o) = -k_{obs}t$

where $[HCrO_4^-]_t$ is the concentration of $HCrO_4^-$ at time t, and

$[HCrO_4^-]_o$ is the initial concentration of $HCrO_4^-$. The absorbance is

directly proportional to concentration if Beer's Law is assumed to

be obeyed, $A = \epsilon lc$. The rate of reaction can be followed by

measuring the increase in the triiodide ion absorbance. Equation

(49) can be changed to terms involving the change of absorbance in

the reaction solution:

(50) $\ln(A_\infty - A_t)/(A_\infty - A_o) = -k_{obs}t$

where A_∞ is the absorbance at infinite reaction time, A_o is the

initial absorbance reading, and A_t is the absorbance reading at time

t. A plot of log $(A_\infty - A_t)$ versus time (t) should be linear with a

slope equal to $-k_{obs}/2.303$. Typical plots obtained from this treat-

ment of the kinetic data are shown in Figure 2. The error limits

reflect an uncertainty of ± 0.002 absorbance units in each DU read-

ing. As the difference between A_∞ and A_t becomes smaller, the

errors naturally become much larger at the end of the reaction.

Figure 2 contains the plot of the data obtained from kinetic

runs at relatively high iodide concentrations (0.100 M) - Graph B -

and low iodide ion concentration (0.0300 M) - Graph A. The straight

line obtained in Graph A indicates first order dependence for two

half-lives. However, Graph B has a linear dependence during the
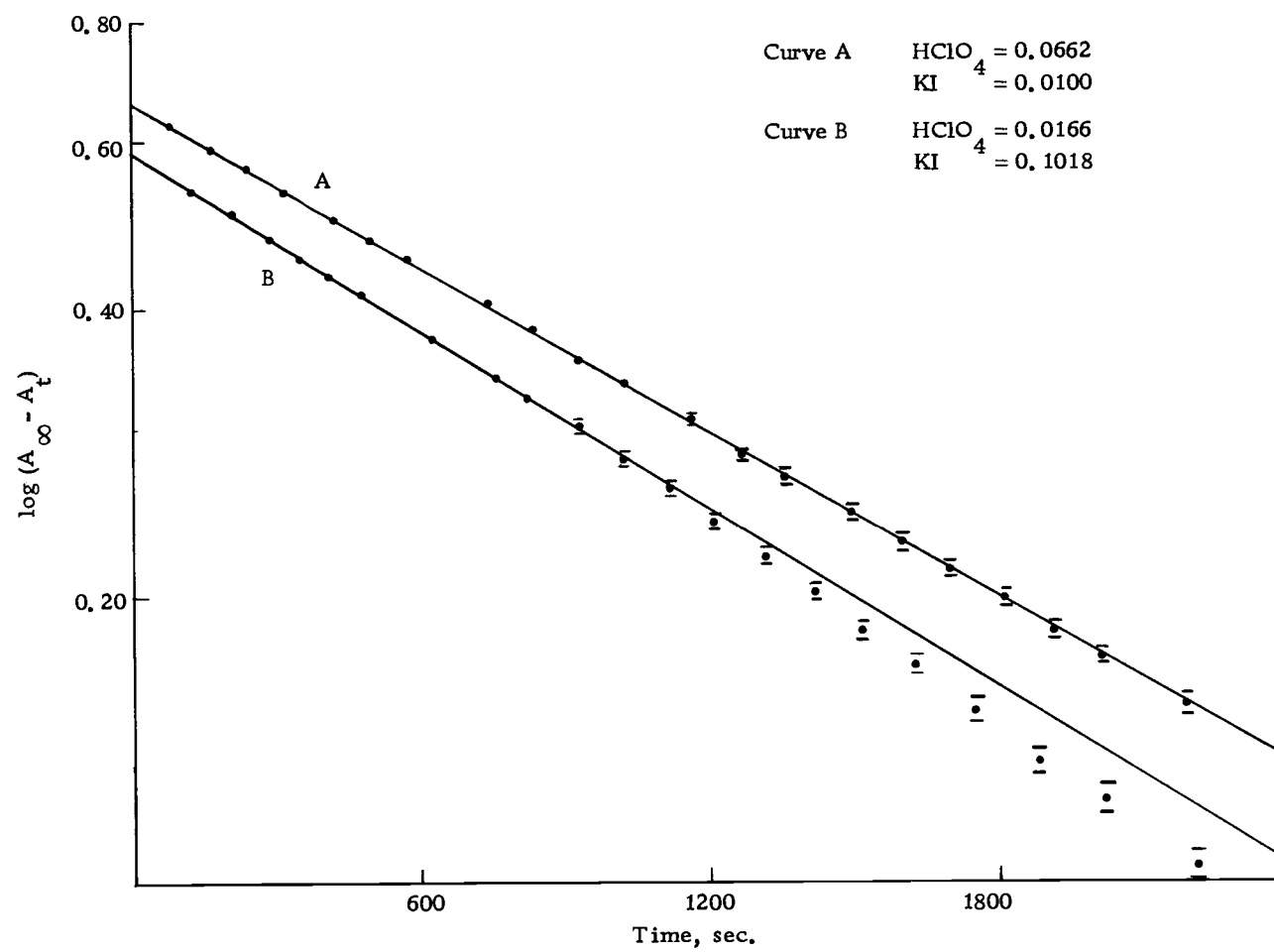
Figure 2. First Order Plots for Data at 20.34° and $\mu = 0.130$ M.

first half-life, and then the data points deviated from a first order

plot. The line drawn in Graph B is through the linear portion of the

plot in which the reaction appears to have first order dependence.

In most kinetic runs the above graphical plots have a linear

dependence from $1\frac{1}{2}$ to 2 half-lives, and Graph B is an extreme

example of this deviation from first order kinetics. The slopes of

these lines drawn through the linear portion of the plots are used to

determine k_{obs} at various iodide and hydrogen ion concentrations,

slope = $-k_{obs}/2.303$. The k_{obs} are therefore taken from approxi-

mately the first 75% of the reaction and the points off this line are

neglected. While the deviation appears in the portion of the graph

with larger error limits, the points are always systematic in pro-

ducing the downcurvature. They are not random around any line.

The k_{obs} measured was reproducible within 3% for three separate

kinetic runs made at the same concentrations $[I^-] = 0.100$ M,

$[H^+] = 0.0116$ M.

The deviation from first order kinetics in all of the kinetic

plots obtained is toward a lower order of reaction than first order

in $HCrO_4^-$. The reaction appears to be going faster with time than

a first-order dependence would predict. A zero-order plot for the

reaction, $(A_\infty - A)/(A_\infty - A_o)$ versus time, yields a continuous curve.

This eliminates it as the reaction order. The linear portion of the

first-order plots indicates that it really is a first-order plot until

later in the reaction when something "happens" or "takes over".

This behavior will be discussed later in the discussion section on

"Deviation from First Order Kinetics".

The dependence of the reaction on $HCrO_4^-$ was further studied

by varying the initial concentration of $HCrO_4^-$. Typical kinetic plots

obtained are shown in Figure 3. Curve C, highest $[HCrO_4^-]_o$, has

a linear portion for the first two to three half-lives. Curve B,

middle $[HCrO_4^-]_o$, has the linear portion for two half-lives before

the deviation begins. Curve A was at the lowest $[HCrO_4^-]_o$ and the

data points appeared to curve near the initial reading. Therefore,

the k_{obs} values for the lower $[HCrO_4^-]_o$, as shown in curve A,

were obtained by drawing a tangent slope through the initial portion

of each reaction. The lines were always drawn to make the slope the

smallest possible. Even these slopes at low $[HCrO_4^-]_o < 10^{-5}$ M

produced values of k_{obs} that were too large in comparison to the

values obtained at high $[HCrO_4^-]_o > 10^{-5}$ M.

The values of k_{obs} found in these experiments for the various

$[HCrO_4^-]_o$ are given in Table 3. In order to compare the runs made

in the various iodide and hydrogen ion concentrations, the values of

k_{obs} were divided by the values of k_{calc}. These values for k_{calc}

were obtained from the rate law which will be given in the "General

Rate Law" section. The ratios, k_{obs}/k_{calc}, are given in Table 3.

The values of these ratios were averaged for each initial chromate

Curve A $[HCrO_4^-]_o$ = 3. 75 x 10^{-6} M
           $HClO_4$ = 0. 0116
           KI   = 0. 1000
           λ = 287. 5 mμ

Curve B $[HCrO_4^-]_o$ = 1. 50 x 10^{-5}
           $HClO_4$ = 0. 0116
           KI   = 0. 1000
           λ = 410 mμ

Curve C $[HCrO_4^-]_o$ = 3. 75 x 10^{-5}
           $HClO_4$ = 0. 0465
           KI   = 0. 0300
           λ = 410 mμ
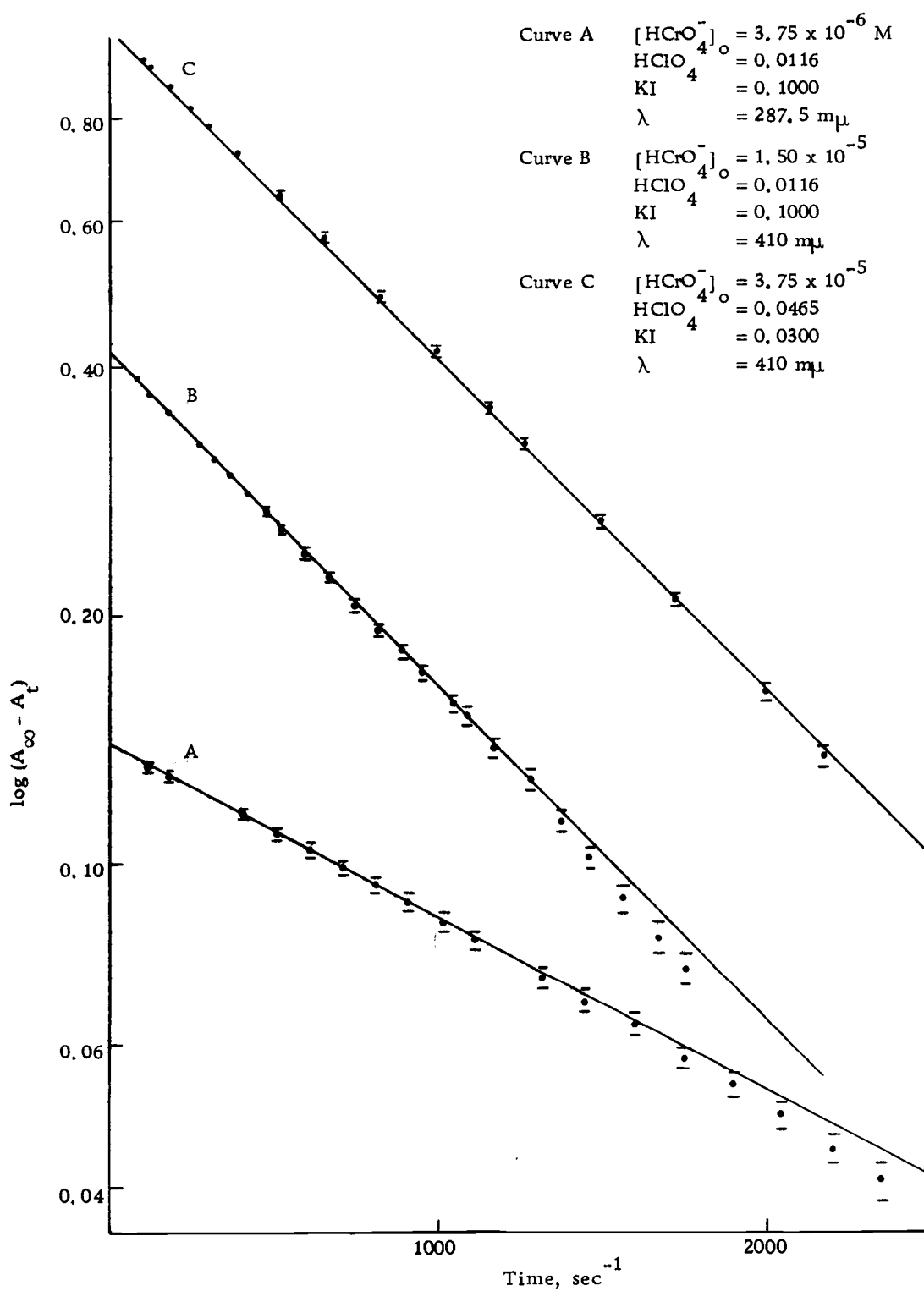
Figure 3. First Order Plots for Various Initial $HCrO_4^-$
Concentrations at 20. 34° and μ = 0. 130 M.

Table 3. The First Order Dependence on Initial Concentration of $HCrO_4^-$ at 20.34° and μ = 0.130 M.

Type of Run	$10^5 [HCrO_4^-]_o$ M	$10^4 k_{obs}$, sec^{-1}	Ratio of k_{obs}/k_{calc}
1a	1.50	4.14	1.07
1a	0.750	5.75	1.49
1a	3.00	3.96	1.05
1b	1.50	3.86	1.00
1b	0.375	4.99	1.30
1b	1.05	3.75	0.98
1b	0.750	4.72	1.23
1b	1.50	4.08	1.06
2b	1.50	9.48	0.98
2b	0.750	10.4	1.08
2b	0.375	11.9	1.25
2c	3.75	9.30	0.97
2c	1.50	10.6	1.00
2c	4.50	9.36	0.98
2c	3.00	9.62	1.00
2c	1.50	9.30	0.98
2c	2.25	9.39	0.98
2b	1.05	9.55	1.00
2b	0.525	10.8	1.08
2b	0.375	10.3	1.08
3a	1.65	5.57	0.98
3b	0.495	6.24	1.10
3a	1.65	5.66	0.99
3a	0.825	6.01	1.05
3a	2.47	5.57	0.98

a. λ = 353 mμ b. λ = 287.5 mμ c. λ = 410 mμ

1. $[H^+]$ = 0.01116 M, $[I^-]$ = 0.1000 M

2. $[H^+]$ = 0.0465 M, $[I^-]$ = 0.0300 M

3. $[H^+]$ = 0.0223 M, $[I^-]$ = 0.0600 M

concentration, and the ratios plotted versus the $[HCrO_4^-]_o$ in

Figure 4. The horizontal line drawn in the figure is the value expected

if the $HCrO_4^-$ followed the first order dependence calculated from the

rate law. An error limit of 5% was assumed for the various points

except for the $[HCrO_4^-]_o = 1.5 \times 10^{-5}$ M. There were six runs made

at this concentration and the error limit was reduced to 3%. The

k_{obs} obtained from the linear portion of first-order plots was

independent of $[HCrO_4^-]_o$ above 1.0×10^{-5} M as shown in Figure 4.

Since, in this study, all the kinetic runs for the rate law were made

with $[HCrO_4^-]_o > 1.4 \times 10^{-5}$ M, the assumption of first order

dependence upon $HCrO_4^-$ appears to be valid.

The large deviations at low $[HCrO_4^-]_o$ were rather erratic

since some runs gave very curved first-order plots and the tangent

line was difficult to draw. Also the change, $A_\infty - A_o$, was not very

great and large errors were obtained for the data points. There-

fore, these lower $[HCrO_4^-]_o$ runs must be regarded as having larger

error limits, > 5%, than the normal $[HCrO_4^-]_o$ runs. The deviation

from first order appeared to be real at very low $[HCrO_4^-]_o$, but

errors encountered in measuring these k_{obs} did not permit further

experimentation. The dotted line drawn in Figure 4 is only an

approximate guide to the deviation observed.

One kinetic run was made with $[HCrO_4^-]_o = 5 \times 10^{-4}$ M, so

that the effect of a large change in $[HCrO_4^-]_o$ could be determined.
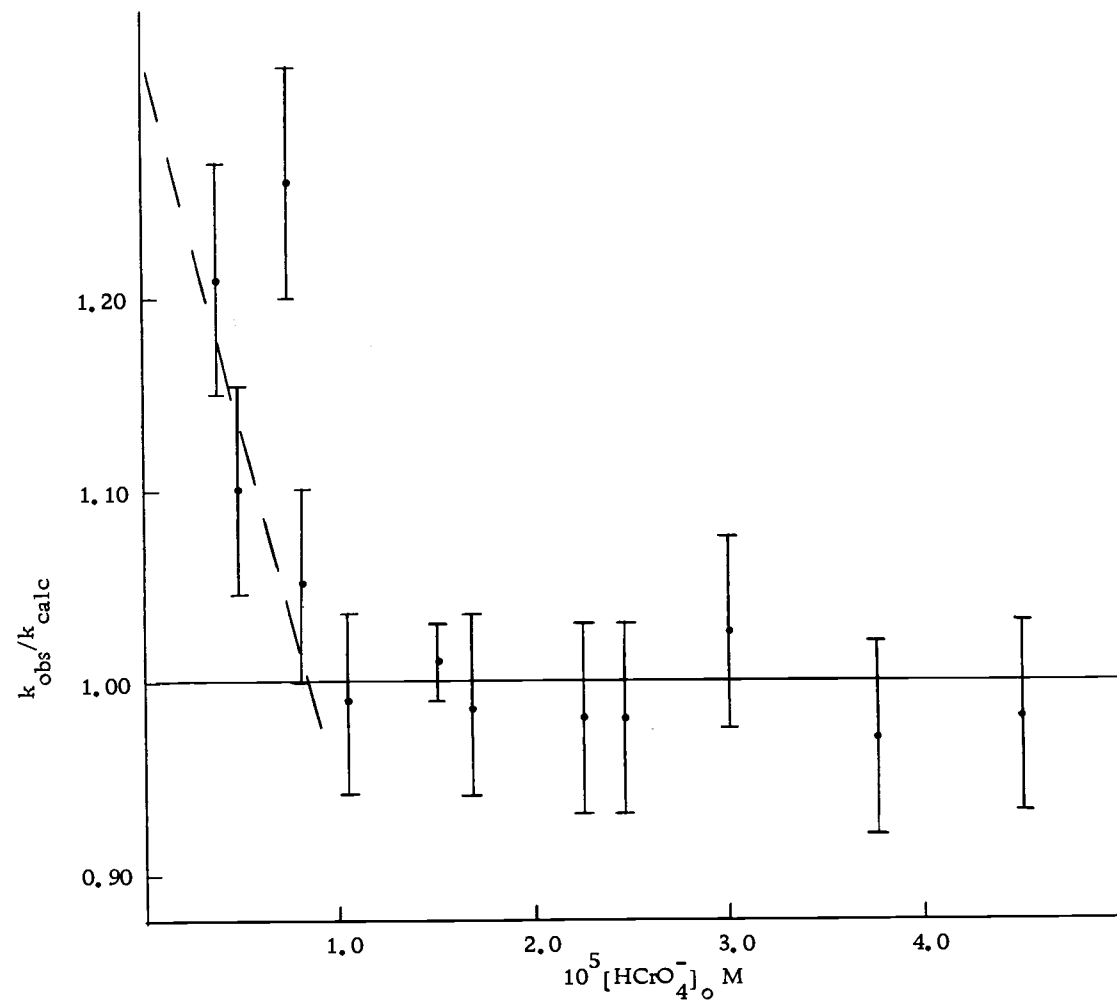
Figure 4.   The Dependence of k_{obs} on the Initial $HCrO_4^-$ Concentration.

The concentrations of hydrogen ion, $[H^+]_o = 0.0438$ M, and iodide

ion, $[I^-]_o = 0.0400$ M, changed by 10% during the reaction. A

limiting tangent line was drawn through the initial reaction points

on a first-order plot of the data. The resulting slope gave a

$k_{obs} = 1.3 \times 10^{-3}$ sec^{-1}. A standard kinetic run with $[HCrO_4^-]_o =$

1.65×10^{-5} M had a $k_{obs} = 1.43 \times 10^{-3}$ sec^{-1}. Therefore, an

increase by a factor of 30 in the initial concentration of $HCrO_4^-$

lowered the reaction rate by 8%. This was not considered to be a

significant change. A tangent line at a fractional-life of 2/3 had a

slope of 1.0×10^{-3}, or a 23% decrease from the initial slope. If

the change in the initial concentrations of $[H^+]$ and $[I^-]$ is taken

into account, there should be a 20% decrease in the slope. The

deviation appears to be entirely due to the concentration change in

the iodide and hydrogen ions during the reaction.

Effect of Products

The deviation of the reaction from first order kinetics in

$HCrO_4^-$ was suggestive of an auto-catalytic reaction. The reaction

was run in the presence of an initial concentration of either tri-

iodide ion or chromium(III) ion. There was no noticeable effect in

the first order plots when triiodide ion was present. There was no

change in k_{obs} within ± 2%. The $Cr(H_2O)_6^{3+}$ was added in an initial

concentration, and again there was no change in the k_{obs} within ± 2%.

These results are listed in Table 4. This latter experiment was more frustrating to carry out than it would appear since the pre-pared $Cr(H_2O)_6^{3+}$ contained $HClO_4$ from its recrystallization. The $[Cr(H_2O)_6](ClO_4)_3$ purchased from the G. Fredrick Smith Co. did not contain a measurable amount of $HClO_4$, but did contain CrO_4^{2-}. This excess CrO_4^{2-} gave an end-point value which was 0.14 absorbance units higher than that expected. While the rate of reaction was unchanged, this increase of triiodide ion was hard to explain until the source of excess CrO_4^{2-} was discovered. It was found that the products did not catalyze the reaction and were not the source of the deviation from first-order kinetics.

Table 4. The Effect of the Products on the Rate of Reaction at 20.34° and μ = 0.130 M.

Initial Concentration	$10^4 k_{obs}$, sec^{-1}
of $[I_3^-]$	
0.00	3.50 (a)
8.40×10^{-5} M	3.59 (a, c)
of $[Cr(H_2O)_6^{3+}]$	
0.00	3.04 (b)
5.46×10^{-3} M	3.00 (b)

(a) $[H^+]$ = 0.0174 M, $[I^-]$ = 0.0600 M, $[HCrO_4^-]_o$ = 1.69×10^{-5} M

(b) $[H^+]$ = 0.0146 M, $[I^-]$ = 0.0800 M, $[HCrO_4^-]_o$ = 1.65×10^{-5} M

(c) λ = 380 mμ

General Rate Law

The k_{obs} which was obtained from the first-order kinetic plots described previously contains the rate dependence on the iodide and hydrogen ion concentrations. In order to determine the dependence of k_{obs} on $[H^+]$ and $[I^-]$, kinetic runs had to be made at various concentrations of these two ions. The combinations of iodide and hydrogen ion concentrations are listed in Table 5. The range of concentrations, $[H^+]$ from 0.0095 to 0.1036 M and $[I^-]$ from 0.0050 to 0.1200 M, is limited in various ways. First, the ionic strength was kept at 0.130 M so neither species could be over a practical limit of 0.120 M. The lower concentration of iodide ion was limited since iodide is necessary for the triiodide ion formation. At the lowest $[I^-]$, 0.005 M, iodine accounted for 20% of the product, and the A_∞ value was decreased by 0.120 absorbance units. These solutions were not very stable, and the A_∞ value tended to decrease after 3-4 hours. This time period was necessary for the measurement of A_∞. The lowest practical limit set for $[I^-]$, 0.005 M. The highest combination of $[H^+]$ and $[I^-]$ that could be used was limited by the rate of reaction; $t_{\frac{1}{2}} > 125$ sec. The lowest combination was set by practical terms of measuring the reaction, and a run with a half-life of approximately 6,000 sec. was the longest run made.

Table 5. The Kinetic Data for the First Order Reaction of $HCrO_4^-$
at 20.34° and $\mu = 0.130$ M.

$10^2[H^+]$, M	$10^2[I^-]$, M	$10^4 k_{obs}$ sec^{-1}	$10^4 k_{calc}$ sec^{-1}
0.941	6.528	1.77	1.74
1.317	6.515	2.76	2.78
1.412	6.506	3.18	3.07
1.882	6.506	4.97	4.80
2.352	6.506	7.09	6.99
2.850	4.998	7.12	6.91
3.800	4.998	13.4	12.1
1.330	4.999	1.85	2.02
0.950	12.00	3.66	3.90
10.36	1.005	20.9	20.5
10.36	1.996	41.5	43.1
10.36	2.646	54.1	59.2
8.632	1.998	25.8	26.6
8.632	2.995	38.2	42.3
8.632	3.999	55.3	59.8
6.905	2.996	25.3	24.1
6.905	5.026	50.7	45.8
5.180	5.005	23.5	23.4
5.180	6.018	28.1	29.9
5.180	7.006	37.1	36.9
3.453	6.995	18.7	15.8
3.453	8.995	23.7	22.7
6.054	0.904	4.63	4.53
6.054	0.703	3.45	3.47
6.054	0.600	2.95	2.93
1.009	10.02	3.68	3.33
1.412	10.02	5.94	5.51
2.018	10.02	10.0	9.87
6.055	0.598	2.90	2.92
6.055	0.901	4.74	4.52
6.055	0.706	3.48	3.48
1.412	4.998	1.99	2.20
1.009	4.998	1.33	1.38
2.018	4.998	3.82	3.80
5.045	0.896	3.02	2.91

Table 5. (Continued)

$10^2 [H^+]$, M	$10^2 [I^-]$, M	$10^4 k_{obs}$ sec^{-1}	$10^4 k_{calc}$ sec^{-1}
5.045	0.998	3.36	3.27
5.045	2.004	7.90	7.14
4.036	1.000	1.99	2.01
7.600	2.999	29.9	30.6
3.453	8.001	18.5	19.1
9.927	3.076	55.0	62.9
9.927	0.996	18.5	18.1
9.927	2.011	38.7	38.8
8.272	1.104	12.4	12.4
8.272	2.997	34.5	38.0
8.272	2.000	23.5	23.8
9.927	0.509	9.49	8.91
9.927	0.598	11.3	10.6
9.927	0.698	13.8	12.5
6.618	1.000	6.47	6.29
6.618	1.001	6.70	6.30
1.660	10.18	7.02	7.29
6.980	0.995	7.14	7.15
5.815	1.003	4.61	4.60
1.628	10.01	6.75	6.90
1.163	9.995	4.10	4.09
1.163	10.00	4.08	4.09
1.163	9.995	3.98	4.09

$[HCrO_4^-]_o = 1.5$ to 2.0×10^{-5} M

S/X = 0.06

$k_1 = 2.06 \times 10^{-1} \pm 0.009$ M^{-2} sec^{-1}

$k_2 = 111 \qquad \pm 7 \qquad$ M^{-4} sec^{-1}

$k_3 = 154 \qquad \pm 3 \qquad$ M^{-4} sec^{-1}

The dependence of the reaction upon the iodide and hydrogen ion concentrations can be ascertained by trying various rate laws. These trials are used to try to correlate the data obtained. The first trial rate law used here was of the form proposed by Beard and Taylor (6).

$$(51) \qquad k_{obs} = k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2$$

A plot of $k_{obs}/[H^+][I^-]$ versus $[H^+][I^-]$ should be linear with a slope equal to k_2 and an intercept of k_1. The resulting graph for the data in Table 5 is shown in Figure 5. For a few selected points this plot could yield some order as is shown by the arbitrary line drawn in Figure 5. These points represent the data taken in the acid range of both Beard and Taylor's and Howlett's studies. However, the iodide ion for these points was between 0.04 and 0.06 M, which is slightly higher than in the earlier studies. This plot could not correlate all of the data in this study, especially for those runs in which $[H^+]$ was much larger than $[I^-]$. The rate law proposed by Howlett, $k[H^+]^2[I^-]^2$, should also be represented by this plot, except the intercept should be zero instead of k_1. This rate law did not fit our data either.

Other rate laws were attempted using the graphical method. The following rate law was tried:
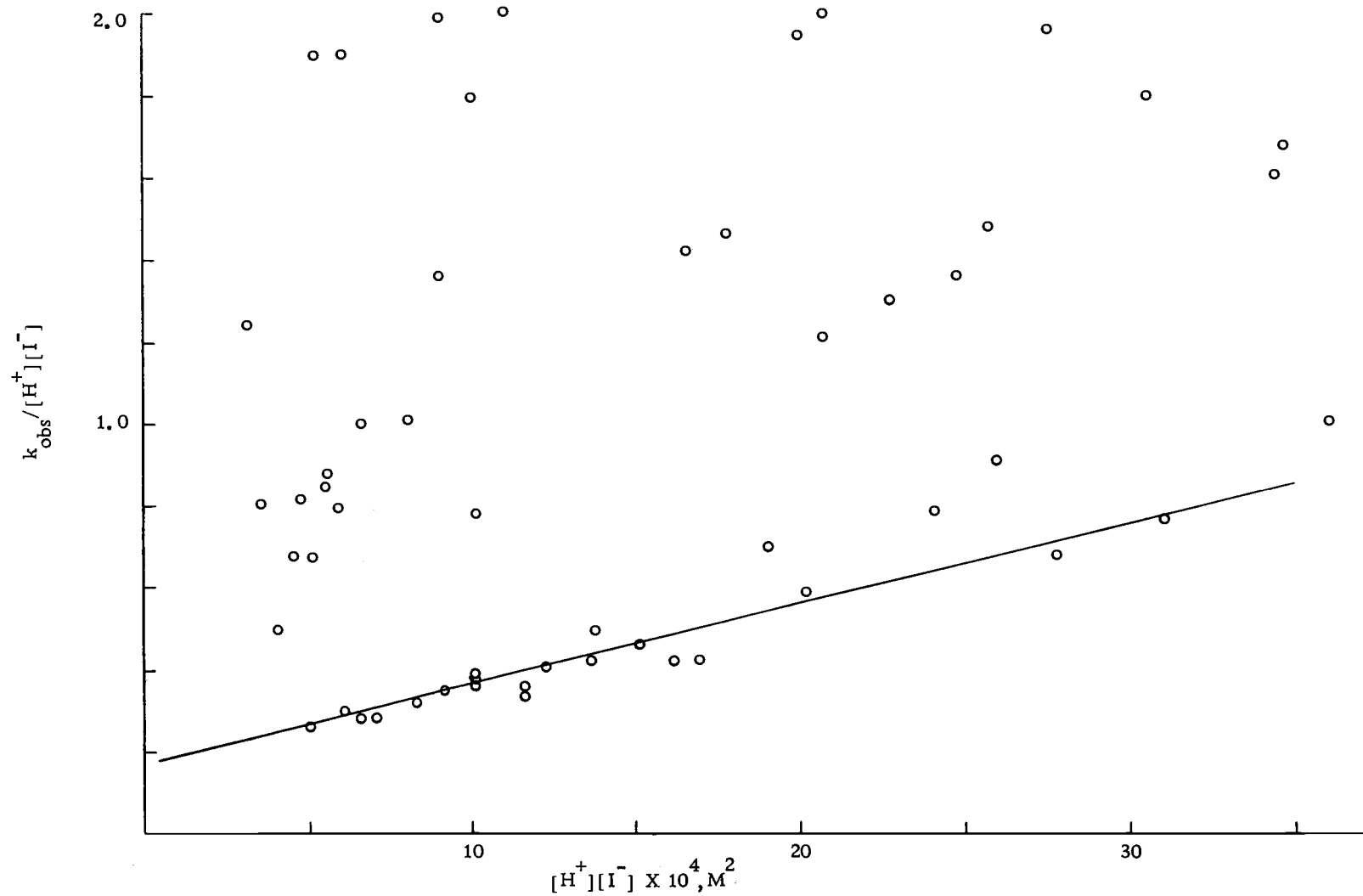
Figure 5. Correlation of k_{obs} by the Rate Law: $k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2$.

$$(52) \qquad k_{obs} = k_1 [H^+] [I^-] + \frac{k_2 [H^+]^2 [I^-]^2}{k' + [I^-]}$$

in which different values of k' were used in a series of graphs.

In these plots, the correlation of the data for $[H^+] < 0.06$ M was

better than for the rate law without a denominator term. However,

the overall correlation was not good and led to scattering of the data.

There was no way of judging the "best" k' value. The high acid runs

were not correlated by these rate laws in any logical manner.

Since the graphical representations of the data were unsuccess-

ful, more complex rate laws were tried by using a computer program.

The program was a least-squares analysis in which one to six

independent variables could be solved. This program was developed

by Professor Lise Hedberg, Oregon State University Computer

Center. The mathematical description of this computer program is

given in the Appendix. The trial rate laws which were tried in order

to correlate the data are shown in Table 6.

There were three criteria used in assessing how well the rate

law correlated the data. The first, and necessary, criterion was to

have a low overall dispersion in the correlation of the data. This

dispersion was defined as:

$$(53) \qquad S = [\Sigma (k_{obs} - k_{calc})^2 (WF)^2 / (n - IV)]^{\frac{1}{2}}$$

where n is the number of independent runs and IV is the number of

Table 6.   Trial Rate Laws to Correlate Kinetic Data.

Trial no.	$k_{obs} =$	*S/X, %
1.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-]$	6.0
2.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-]^2$	26
3.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-] + k_3[H^+]^3[I^-]^2$	13
4.	$k_1[H^+][I^-]^2 + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-]^2$	46
5.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-] + k_3[H^+]^2[I^-]^2$	13
6.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-] + k_3[H^+][I^-]^2$	12
7.	$k_1[H^+][I^-]^2 + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-]$	14
8.	$k_1[H^+][I^-] + \dfrac{k_2[H^+]^2[I^-]^2}{k' + [I^-]} + k_3[H^+]^3[I^-]$	
9.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2 + \dfrac{k_3[H^+]^3[I^-]^2}{k' + [I^-]}$	
10.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-] + k_3[H^+]^2[I^-]^2 + k_4[H^+]^3[I^-]$	5.9
11.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-] + k_3[H^+][I^-]^2 + k_4[H^+]^2[I^-]^2$	----

*S/X = the percent of dispersion for the rate law.

independent variables in the rate law. The k_{obs} has the same meaning previously given, and k_{calc} is the first order rate constant calculated using the k_i values ($k_i = k_1, k_2, \ldots$) found in the various rate laws. The $WF = X/k_{obs}$ is a weighting factor employed to compare all runs to the same value. The X is equal to 1.0×10^{-3} in all of the rate law trials. This weighting factor was necessary so that the least-squares program would give comparable weight to the slow kinetic runs. The values of k_i did not depend upon the value of X used in defining the WF. However, the S measurement did depend on the value chosen. The more useable dispersion expression is S/X which remains constant with different values for X. The ratios, S/X, for the different rate laws are listed in Table 6.

The second criterion was that negative rate constants would have no physical meaning. Any rate law that produced a negative k_i value was omitted from further consideration. The rate laws in Table 6 which gave negative k_i values were numbers 2, 4, 6, and 11. The third criterion was that any rate law which resulted in a trend in the fitting of the data over a range of concentrations was omitted. The S/X value could be low, but the rate law might only fit the low acid runs well but not the high acid runs. An example of this trend was found in trial 5 of Table 6, in the series of runs in which $[I^-] = 0.020$ M.

$[H^+]$, M	Percent error
0.05045	2.4
0.08272	5.8
0.09927	16.7
0.1036	15.9

Using the above criterion, the three-term rate law which correlates the data best is number 1 of Table 6.

$$(54) \quad k_{obs} = k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-]$$

This rate law gave the lowest S/X value by almost a factor of two. Using the first criterion, this rate law would be chosen over the others. There were no trends noticed in the correlation of the data by this rate law. The actual form of the rate law had to be specific since a variation in one exponent gave a much larger S/X.

The rate constants for this rate law are:

$k_1 = 0.206 \pm 0.009 \ M^{-2} sec^{-1}$, $k_2 = 111 \pm 7 \ M^{-4} sec^{-1}$, and

$k_3 = 154 \pm 3 \ M^{-4} sec^{-1}$. The standard errors for the different k_i values are calculated as shown in the Appendix. The S/X value is 0.0596 so the percent of deviation in the rate law is approximately 6%. The correlation of the values of k_{obs} by this rate law is shown in Figure 6 where a plot of $k_{obs}/[H^+][I^-]$ versus $(111[H^+][I^-] + 154[H^+]^2)$ is made. The predicted line for the rate law is shown with an intercept of 0.206 and a slope of 1.00.

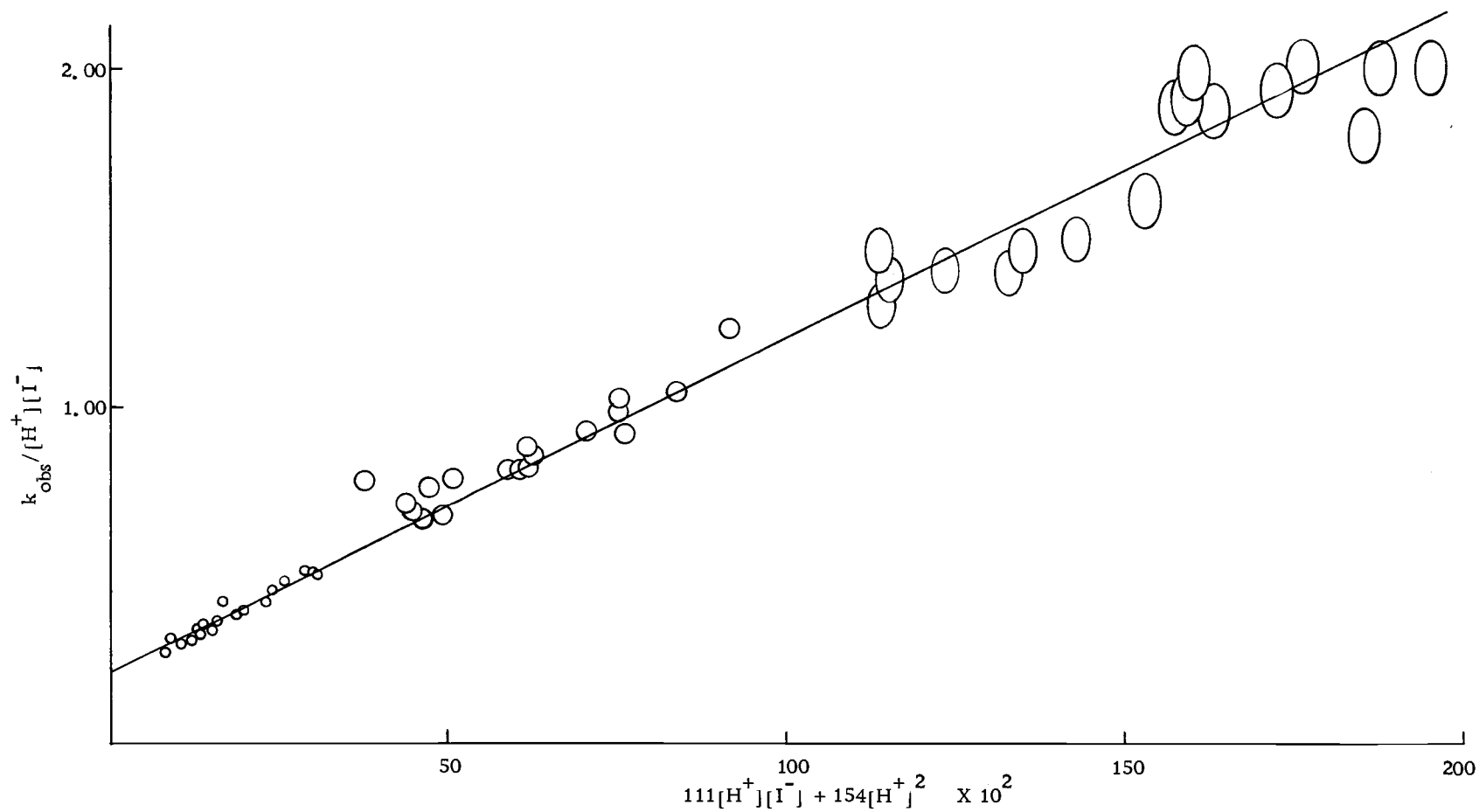The rate laws, numbers 8 and 9, were tried to determine if a

Figure 6. Correlation of k_{obs} by the Rate Law: $0.206[H^+][I^-]$
$+ 111[H^+]^2[I^-]^2 + 154[H^+]^3[I^-]$.

denominator term was present. Seven values of k' were chosen over the range 1.00 to 0.001. The S/X values are not listed since they varied with each k' trial. As k' was varied there was no minimum observed in the S/X values. Thus, the S/X for k' = 0 was always the largest value obtained, and S/X for k' > $[I^-]$ was the smallest value obtained. Thereby, no denominator term were justified by our kinetic data.

Rate laws containing more than three terms were tried in order to better correlate the data. Since a four-termed rate law should fit the data better, any that did not were disregarded. Trial number 10 did correlate the data as well as the above three-term rate law. The argument against this form was that the fourth term did not reduce the error significantly over the three term rate law. The fourth term only decreased S/X by 0.0012. The constants for the four term rate law are: $k_1 = 0.181 \pm 0.012 \ M^{-2} sec^{-1}$, $k_2 = 1.87 \pm 0.80 \ M^{-3} sec^{-1}$, $k_3 = 108 \pm 7 \ M^{-4} sec^{-1}$, and $k_4 = 134 \pm 9 \ M^{-4} sec^{-1}$. The k_2 term has a very large error associated with it, 42%, while the others were all less than 10%. It can be concluded that this extra term is undefined and is used only for "curve fitting" in the program. Other trials with more than three terms, up to six, were attempted. These rate laws gave negative rate constants and were therefore eliminated. Nothing seemed to be gained by including additional terms. The data was well accounted for in a three term rate law and might not be

large enough in range to detect an additional term, if indeed there

was one. As was stated earlier, the actual form of the three terms

must be specific in order to have a low S/X value, all positive k_i

values, and well defined k_i values, as judged by the standard errors.

Therefore, the rate law is considered to be related to the chromate-

iodide system and is not just a mathematical expression for predic-

tions of k_{obs}.

Effect of Oxygen

The effect of oxygen upon the chromate-iodide reaction is

important. It is known that some oxidation of iodide ion by oxygen

takes place even in the N_2-flush runs. The main problem caused by

oxygen is the uncertainty in the measured absorbance of the solution

at infinity reaction time, A_∞. The oxidation of iodide by oxygen

produces more triiodide ion than could come from the initial chromate

concentration. Likewise, the A_∞ would increase with time since the

oxygen-iodide reaction continues after the chromate-iodide reaction

approaches equilibrium.

The N_2-box condition was used to minimize the incursion of

oxygen during handling of the reactant solutions. Sixteen runs were

made in this condition, and the results of these kinetic runs are listed

in Table 7. Several trial rate laws were tried to see if the values of

k_{obs} could be best represented by the general rate law previously

Table 7. First Order Rate Constants for the N_2-box Condition at 20.34° and $\mu = 0.130$ M.

$10^2[H^+]$, M	$10^2[I^-]$, M	$10^4 k_{obs}$, sec^{-1}	$10^4 k_{calc}$, sec^{-1}
1.00	10.01	3.48	3.48
1.00	7.00	1.89	2.10
2.00	6.00	4.63	5.16
2.00	4.02	3.20	2.94
3.99	1.00	1.96	1.99
3.99	3.00	7.88	7.51
3.00	3.01	4.31	4.20
3.00	5.00	7.97	8.42
5.99	1.00	4.79	5.17
5.99	0.700	3.50	3.50
3.79	2.00	4.84	4.03
1.90	10.00	1.05	1.02
0.95	10.00	3.62	3.21

$[HCrO_4^-]_o = 1.15 - 1.97 \times 10^{-5}$ M

$S/X = 0.09$

$k_1 = 0.170 \pm 0.038$ M^{-2} sec^{-1}

$k_2 = 161 \pm 35$ M^{-4} sec^{-1}

$k_3 = 166 \pm 14$ M^{-4} sec^{-1}

found. These trials are listed in Table 8. The rate laws 4 and 5 were

tried with various k' between 1.0 and 0.001. No minimum S/X value

was obtained for these values of k' and no denominator term was

justified by the data. The S/X of trial 1 was much less than the other

trials. The rate law is again designated to be:

$$(55) \qquad k_{obs} = k_1 [H^+][I^-] + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-]$$

The values for each k_i were calculated to be: $k_1 = 0.175 \pm 0.038$ M^{-2}

sec^{-1}, $k_2 = 161 \pm 35$ $M^{-4} sec^{-1}$, $k_3 = 166 \pm 14$ $M^{-4} sec^{-1}$. The k_1

and k_3 values were within a standard deviation from the k_i values

found in the N_2-flush study. The k_2 term was definitely larger.

Table 8. Trial Rate Laws to Correlate the Kinetic Data in the N_2-box Condition.

Trial	$k_{obs} =$	[*]S/X, %
1.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2 + k_3[H^+]^3[I^-]$	9.2
2.	$k_1[H^+][I^-] + k_2[H^+]^3[I^-]$	20.2
3.	$k_1[H^+][I^-] + k_2[H^+]^2[I^-]^2$	25.
4.	$k_1[H^+][I^-] + \dfrac{k_2[H^+]^2[I^-]^2}{k' + [I^-]} + k_3[H^+]^3[I^-]$	
5.	$k_1[H^+][I^-] + \dfrac{k_2[H^+]^2[I^-]^2}{k' + [I^-]}$	

[*]S/X = the percent of dispersion for the rate law.

The oxygen problem of increasing A_∞ value was largely stopped with this technique. However, after the solution had remained in the cell for a few hours, the A_∞ values started to increase slowly. There were other problems associated with this technique. One problem concerned temperature control inside the N_2-box. The initial reaction temperature needed to be the same as the temperature inside the DU cell-holder. By the time the cell, which was not at the DU temperature, was filled with reactants and transferred from inside the box to the DU spectrophotometer, the initial reaction temperature could be $\pm 1°$ from the DU temperature. Another problem was the time involved in transferring the cell from the inert-atmosphere box to the spectrophotometer. This time was 150-200 sec. with no assistance, and 60-100 sec. if someone else took the first reading. The rate of reaction that could be studied had a practical limit, $t_{\frac{1}{2}} > 600$ sec. The N_2-box condition was very difficult in which to work, had very poor initial temperature control, and was limiting in the concentration range for fast reactions. Because of these difficulties, the values of k_{obs} obtained in the N_2-flush were felt to be better, and only runs made in the N_2-flush condition were used in the determination of the rate law.

The kinetic runs made using the vacuum line technique gave very constant A_∞ values, and seemed to have solved this problem completely. The k_{obs} values obtained from these runs were in

agreement with the k_{calc} values which would be predicted using the values of k_i from the N_2-flush rate law. Shown below are the results for these runs at 20.4° and $[HCrO_4^-]_o = 1.65 \times 10^{-5}$ M.

$10^2[H^+]$ M	$10^2[I^-]$ M	$10^4 k_{obs}$, sec^{-1}	$10^4 k_{calc}$, sec^{-1}
6.698	1.001	6.56	6.46
1.116	11.00	4.56	4.38
2.233	6.002	5.34	5.60

If the values for k_i were used from the N_2-box study instead of the N_2-flush study, the difference in $k_{obs} - k_{calc}$ was much greater. Therefore, the rate constants from the N_2-flush runs were assumed to be correct. Because of the constant A_∞ values of the vac-line runs, the end-point problem could be due mainly to dissolved oxygen in the system. Oxygen seepage into the cell appeared to be a minor problem. The main observation in the vacuum-line runs was that the graphical first order plots of the kinetic runs show the same curvature noted earlier. Therefore, the curvature is not due simply to oxygen.

In order to complete the oxygen effect study, conditions were tried in which the oxygen content was purposely made higher than that found in the N_2-flush runs. The conditions of an atmospheric mixture of N_2 and O_2, and the O_2-flush were made to see if any qualitative differences in the kinetic runs could be noted. It was observed that after the kinetic run had been corrected for the oxygen-iodide reaction,

the k_{obs} values obtained were approximately the same as those found

under other conditions, Table 9. However, the A_∞ values were not

the same. Even if the A_∞ was corrected using the H^+-I^- blank,

triiodide produced from the H^+-O_2-I^- reaction, it was still too large

to be accounted for by the production of I_3^- from $HCrO_4^-$. It appeared

as if excess triiodide ion were produced from the reaction. The dif-

ferent oxygen conditions that were tried are listed in Table 10. They

are arranged so that the oxygen content increases as one reads down

the table. The values are reported as the theoretical amount of tri-

iodide expected from the chromate reaction, Theor. $[I_3^-]_\infty$, and the

amount of triiodide observed at the end of reaction, $Obs[I_3^-]_\infty$, after

correcting for the triiodide produced in the $O_2 + I^- + H^+$ blank. The

ratio of these two amounts is listed in the last column to show the

relative excess of triiodide produced. The excess triiodide ion

produced depended upon the concentration of the oxygen in the solution

since the ratio increases as the oxygen content of the solution

increases. It should be noted once again that only runs made in the

N_2-flush condition were used to determine the k_1, k_2, and k_3 values

in the general rate law.

Ionic Strength

The dependence of the reaction upon the ionic strength was

studied at one set of iodide and hydrogen ion concentrations. This

Table 9. Values of k_{obs} Measured at Various Oxygen Conditions at 20.34° and $\mu = 0.130$ M.

	N_2-box $10^4 k_{obs}$, sec^{-1}	Atm. $10^4 k_{obs}$, sec^{-1}	O_2-flush $10^4 k_{obs}$, sec^{-1}	k_{calc} 10^4, sec^{-1}
1.	----	3.66	3.98	4.06
2.	3.51	3.13	3.54	3.04
3.	10.4	9.00	8.90	8.87

1. $[H^+] = 0.0116$ M, $[I^-] = 0.100$ M, $[HCrO_4^-]_o = 1.15 \times 10^{-5}$ M

2. $[H^+] = 0.0095$ M, $[I^-] = 0.100$ M, $[HCrO_4^-]_o = 1.15 \times 10^{-5}$ M

3. $[H^+] = 0.0190$ M, $[I^-] = 0.100$ M, $[HCrO_4^-]_o = 1.15 \times 10^{-5}$ M

Table 10. Excess Production of Triiodide Ion with Increasing Oxygen Concentration at 20.34° and $\mu = 0.130$ M.

Condition	$[I^-]$, M	$[H^+]$, M	Theor. $10^5 [I_3^-]_\infty$	Obs. $10^5 [I_3^-]_\infty$	Ratio obs./theor.
Vac-line	0.0100	0.0878	2.22	2.22	1.00
	0.1100	0.0223	3.71	3.71	1.00
N_2-box	0.0200	0.0379	1.61	1.61	1.00
	0.1000	0.0095	1.73	1.74	1.00
N_2-flush	0.01	0.0190	1.87	1.87	1.00
	0.1000	0.0100	2.10	2.18	1.04
Air	0.02	0.0380	1.62	1.69	1.04
	0.1000	0.0095	1.73	1.86	1.07
O_2-flush	0.02	0.0190	1.62	1.73	1.07
	0.1000	0.0095	1.73	2.13	1.23

study was made to show in general how the reaction depended upon its surrounding ionic media. A detailed study of how the individual k_i values in the rate law depended upon the ionic strength would require at least twenty kinetic runs at each ionic strength value. This number of runs would make a detailed study of the ionic strength an arduous task. At least four different ionic strength points would have to be included; therefore, a minimum of eighty runs would have been needed for this study.

The mechanisms that have been postulated for the reaction contain many equilibrium steps before the rate determining step is reached. Before anything can be stated about the effect of ionic strength on the rate determining step, the values of these pre-equilibrium constants and their variations with ionic strength must be known. For example, the charges on the species in the rate determining step cannot be determined without knowledge of the pre-equilibrium constants. The main benefit from a study of this type would be the ability to predict the rate of reaction at an ionic strength other than 0.130 M.

The results of the study which was made are listed in Table 11 with the concentrations of iodide and hydrogen ions. A plot of log k_{obs} versus the square root of the ionic strength, $\mu^{\frac{1}{2}}$, is shown in Figure 7. The plot is linear up to $\mu^{\frac{1}{2}} = 0.8 \, M^{\frac{1}{2}}$, and has a minimum at around $0.9 M^{\frac{1}{2}}$. Similar dependence of this reaction upon ionic
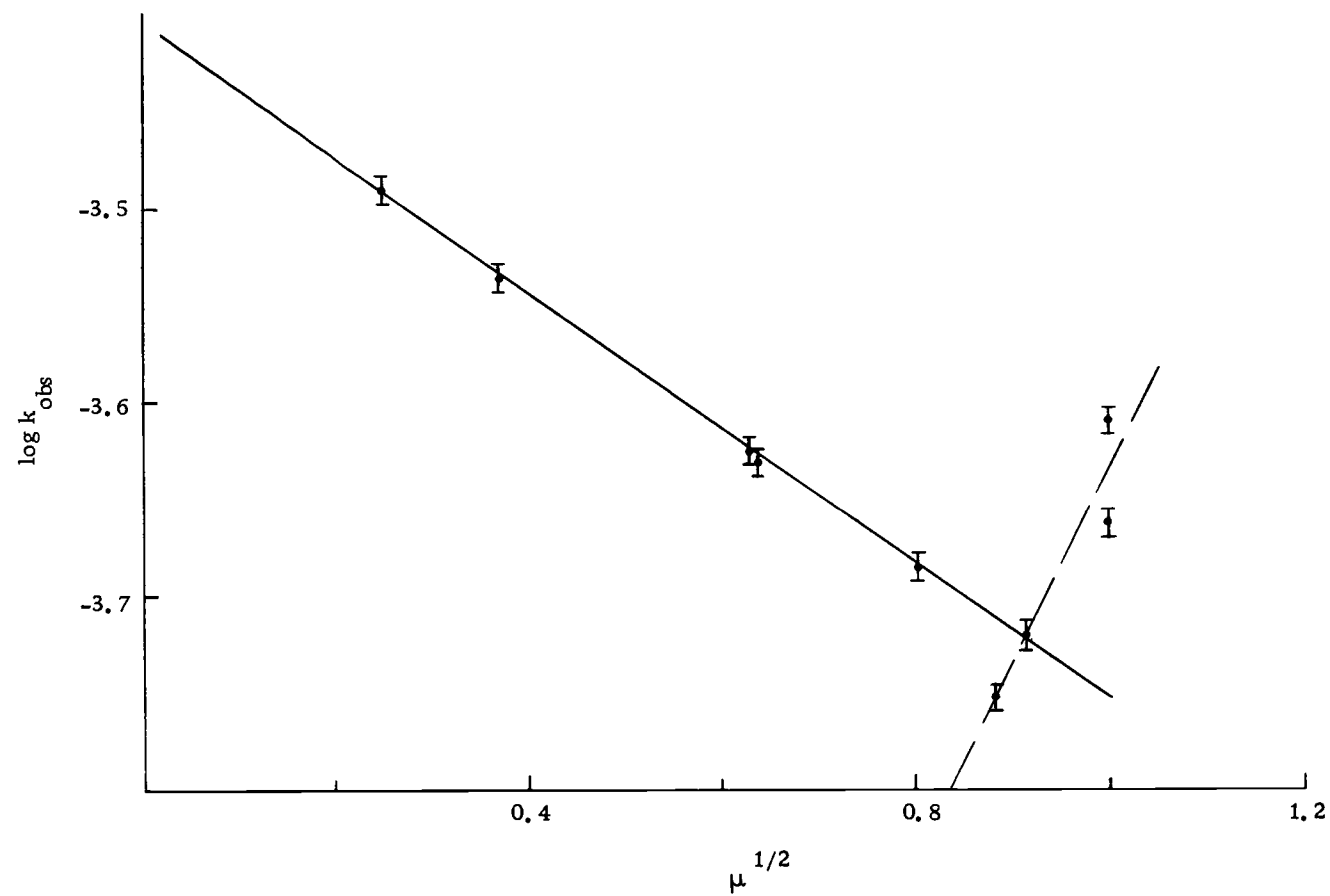
Figure 7. The Dependence of k_{obs} on the Ionic Strength.

strength is also noted in Beard and Taylor's (6) study as well as the

more recent study by Howlett (36).

Table 11. The variation of k_{obs} with Ionic Strength Using KNO_3 as the Neutral Salt at 20.34°.

Ionic Strength $\times 10^1$, M	$\mu^{\frac{1}{2}}$	$10^4 k_{obs}$, sec^{-1}
0.6223	0.249	3.20
1.303	0.361	2.92
1.412	0.375	2.83
3.976	0.631	2.37
4.004	0.632	2.35
6.400	0.800	2.07
7.618	0.873	1.77
8.310	0.912	1.91
9.969	0.998	2.18
10.00	1.000	2.44

$[HCrO_4^-]_o = 1.68 \times 10^{-5}$ M, $[H^+] = 0.0222$ M, $[I^-] = 0.0400$ M.

The salt used to maintain the ionic strength in this study was

KNO_3, since the solubility of $KClO_4$ limits the region of study to that

below 0.130 M. Because of the iodide and hydrogen ion concentra-

tions, the study could not be made below $\mu = 0.06$ M. Runs using

KNO_3 did not differ from kinetic runs in which $KClO_4$ was used.

Therefore, the type of anion did not have an effect upon the reaction

rate. In some runs the potassium ions were replaced with sodium

ions, and again no effect was observed. The results of this study at

20.34° with $[H^+] = 0.0332$ M, $[I^-] = 0.0250$ M, $[HCrO_4^-]_o = 1.4 \times 10^{-5}$ M, and $\mu = 0.250$ M were:

$[K^+]$, M	$[Na^+]$, M	$10^4 k_{obs}$, sec^{-1}
0.2168	0.000	3.43
0.025	0.1922	3.48
0.000	0.2169	3.29

Since Beard and Taylor's (6) study differed from the present study in the ionic strength and the salt used to maintain it, a comparison run using their conditions was made. Three solutions were made, one at 1.5 M ionic strength using NaCl, the second at 1.5 M using NaNO$_3$, and the third one at 0.130 M using KClO$_4$. The results of this study at 20.4° with $[H^+] = 0.0170$ M, $[I^-] = 0.0600$ M, and $[HCrO_4^-]_o = 1.69 \times 10^{-5}$ M were:

| [NaCl], M	μ, M	$10^4 k_{obs}$, sec^{-1}
1.42	1.500	8.16
0.00	1.500 (NaNO$_3$)	3.59
0.00	0.130 (KClO$_4$)	3.72

The value of the 1.5 M NaNO$_3$ run comes close to the run containing 0.130 M KClO$_4$. The ionic strength curve shows qualitatively that these two different salt concentrations should give close to the same values. The rate of the 1.5 M NaCl run is over twice that of the 1.5 M NaNO$_3$ run. The chloride ion must affect the reaction in

some manner. There are two possible causes for this behavior.

The chloride ion could be a catalyst for the chromate-iodide reaction,

or at this high salt solution the effect could be due to a specific anion

interaction. This topic will be developed further in the next section.

The result of the 1.5 M NaCl run is in general agreement with Beard

and Taylor's (6) study. No direct comparison is possible since their

study is also at a different temperature, 25°.

Reaction in the Presence of Added Halide

The interaction of halide ions with the monohydrogen chromate

species should provide some information about the reactivity of

halides with chromate. The reaction

$$(56) \quad H^+ + HCrO_4^- + Cl^- \rightleftharpoons ClCrO_3^- + H_2O \quad K = 11 \text{ M}^{-2}$$
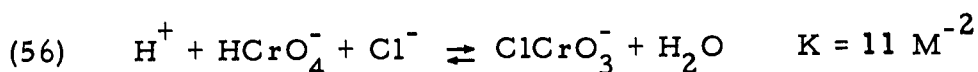
is discussed in the introduction. The $K = 11$ M^{-2} measured by Tong

and Johnson (60) will be used. If the $ClCrO_3^-$ rather than the $HCrO_4^-$

is more reactive toward iodide ion, the rate of reaction should be

increased when appreciable concentrations of Cl$^-$ are added. Or

vice versa, if the $ClCrO_3^-$ species is actually less reactive than

$HCrO_4^-$, the rate of reaction should be decreased. The study made

at 1.5 M NaCl indicates that the chloride does increase the rate and

that this increase may be due to $ClCrO_3^-$.

Kinetic runs made with chloride ions and bromide ions present

are listed in Table 12. It was indicated by these results that the

chloride and bromide ions did not have much influence upon the

chromate-iodide reaction. Using $K = 11$ M^{-2}, the $ClCrO_3^-$ should have

accounted for 10% of the total chromate concentration in the highest

Cl^- concentration kinetic run. This concentration should have pro-

duced a sizeable effect if chloride did affect the reaction. The result

which was observed in the 1.5 M NaCl run could still be either a

catalytic effect or a specific ion effect. The latter reason gains sup-

port from this study at lower ionic strength concentrations.

Table 12. The Effect of Cl^- and Br^- on the Rate of Reaction at 20.34°
and $\mu = 0.130$ M.

$10^2[I^-]$, M	$10^2[Cl^-]$, M	$10^2[Br^-]$, M	$10^4 k_{obs}$, sec^{-1}
1.00	0.00		6.46
1.01	2.68		6.35
1.00	5.37		6.35
2.50	19.2		3.43 (a)
1.00		0.00	6.59
1.00		2.73	6.24
1.00		5.41	6.24

$[HCrO_4^-]_o = 1.50 \times 10^{-5}$ M, $[H^+] = 0.0662$ M

(a) $[H^+] = 0.0332$ M, $k_{calc} = 3.30 \times 10^{-4}$ sec^{-1} after correction for
difference in ionic strengths.

Scavengers for Reaction Intermediates

The subject of induced oxidations in chromate reductions was discussed in the introduction. These induced effects can provide information about the reaction after the rate determining step.

The Mn(II) ion was added to the reaction in order to remove any Cr(IV) which might be produced during the reaction. As discussed earlier, the effect of added Mn(II) upon the Westheimer mechanism is two-fold; MnO_2 should be produced, and the rate of chromate disappearance should be decreased by a factor of two. The results for the chromate-iodide reaction with Mn(II) ion added are listed in Table 13. Kinetic runs with and without added Mn(II) ion were made at the same time for comparison purposes. At the maximum ratio, $[Mn(II)]/[HCrO_4^-]_o = 2 \times 10^3$, no difference in the k_{obs} was noticed from a run made containing no Mn(II) ion. In the experiments with KI = 0.100 M the rate was 8.5% lower in a run with added Mn(II) ion than in a run without added Mn(II) ion. If the k_{calc} from the general rate law is used to give the value of the first order rate constant, then the Mn(II) ion runs do not show any decrease in rate, $k_{calc} = 4.10 \times 10^{-4}$ sec^{-1}. Therefore, the decrease in rate observed for these two Mn(II) ions runs is not considered significant, and, in fact, the measured k_{obs} without the Mn(II) ion may be the value in error. The kinetic first order plots for the runs with added Mn(II)

ion did not differ in any significant way from runs made without Mn(II)

ions. The deviations from first order plots in the Mn(II) runs

occurred at approximately the same half-lives, $t_{\frac{1}{2}} = 2$, as the runs

without Mn(II).

Table 13. The Effect of Added Mn(II) Ion on the Rate of Reaction at 20.34° and $\mu = 0.130$ M.

$10^2[H^+]$, M	$10^2[I^-]$, M	$10^2[Mn(II)]$, M	$10^4 k_{obs}$, sec^{-1}
2.33	7.00	0.000	7.40
2.33	7.06	0.162	7.52
1.16	10.00	0.00	4.50
1.16	10.00	0.448	4.16
1.16	10.00	1.023	4.10
1.74	6.01	0.00	3.98
1.74	6.01	3.46	3.91

$[HCrO_4^-]_o = 1.69 \times 10^{-5}$ M

Manganese(III) ion was investigated to determine if it could be

used as a scavenger for Cr(IV) or I_2^- in place of the Mn(II) ion. The

reaction between Mn(III) ion and iodide ion was first studied in order

to determine if the two could exist in solution together. The concen-

trations in this experiment were $[H^+] = 0.57$ M, $[I^-] = 0.06$ M, and

[Mn(III)] approximately 10^{-5} M. By the time the Mn(III) solution was

mixed with the iodide solution and the first absorbance was taken, the

reaction had gone to completion (61 sec.). If the reaction were

assumed to have completed five half-lives, 97% of the total reaction,

during the mixing and first recording, then the $t_{\frac{1}{2}}$ of this reaction was

at the most 12 sec. and is probably much less. Therefore, the Mn(III)

could not be used to help elucidate the mechanism of the $HCrO_4^-$-

iodide reaction. It did show that the Mn(III) reacts rapidly with the

iodide ion at this acidity.

(57) $$2Mn(III) + 2I^- \rightarrow 2Mn(II) + I_2$$
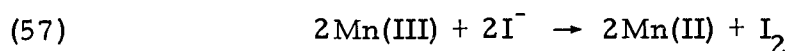
Benzaldehyde has been reported by Wiberg and Richardson (69,

70) to react rapidly with the intermediate species Cr(IV). Benzalde-

hyde was added to see if it could compete for the Cr(IV) intermediate

produced in our kinetic study. The rate of the Cr(VI)-iodide reaction

was not affected by the presence of benzaldehyde, Table 14. There

was no qualitative change in the deviation in the first order rate

plots. The downcurvature started at approximately the same frac-

tional life as in a run without added benzaldehyde. There seemed to

be no oxidation power lost to the benzaldehyde. The increase in the

absorbance corresponded to a stoichiometric amount of triiodide

being produced by the $HCrO_4^-$, after accounting for an initial produc-

tion of triiodide from an impurity in the benzaldehyde. The impurity

in the benzaldehyde always gave a rapid reaction, complete in 100

sec. with the iodide ion, to produce the triiodide ion. The half-life

of this reaction was calculated to be less than 20 sec. by the same

method employed in the Mn(III)-iodide reaction. The impurity

responsible for the pre-oxidation of iodide was probably benzoyl

peroxide. This compound forms from the reaction of benzaldehyde

and oxygen. To insure complete reaction of this impurity, the

benzaldehyde was added to the starting potassium iodide solution.

The impurity produced approximately 5×10^{-6} M of triiodide ion.

The first-order plots of the $HCrO_4^-$-iodide reaction did not show any

effect due to this pre-oxidation of iodide ion. Even after purification,

the benzaldehyde gave this initial iodide to iodine reaction.

Table 14. The Effect of Benzaldehyde and Allylacetate on the Rate of Reaction at 20.34° and $\mu = 0.130$ M.

Chemical	Concentration $\times 10^3$, M	$10^4 k_{obs}$, sec^{-1}	$10^4 k_{calc}$, sec^{-1}
Benzaldehyde	8.70 (a)	4.54	4.56
	5.95 (b)	6.81	6.88
Allylacetate	9.25 (c)	4.12	
	0.00 (c)	3.54	
	4.60 (d)	3.60	
	0.00 (d)	3.04	

$[HCrO_4^-]_o = 1.65 \times 10^{-5}$ M

(a) $[H^+] = 0.0581$ M, $[I^-] = 0.0100$ M

(b) $[H^+] = 0.0163$ M, $[I^-] = 0.1000$ M

(c) $[H^+] = 0.0100$ M, $[I^-] = 0.1000$ M

(d) $[H^+] = 0.0146$ M, $[I^-] = 0.0802$ M

An unsaturated hydrocarbon was a possible reactant for unstable intermediates that could be produced in the chromate reduction. An olefin that was soluble in water and would not react directly with either reactant or product was needed. Allylacetate appeared to be a good choice. However, the kinetic runs with added allylacetate, Table 14, were 17-18% faster than runs without allylacetate. No effect on the curvature of the first order plots was noticed. In a run in which the allylacetate was added to the starting chromate solution, only a third of the total expected iodine was produced. An interaction or reaction between allylacetate and chromate must take place and produce the increase in rate. Since the effect was probably not due to an intermediate, no further investigation of this system was done.

Temperature Studies

In order to determine the temperature dependence for each of the three individual rate constants, the reaction was studied at three temperatures, 10.37°, 20.34° and 29.67°. Since three rate constants had to be determined at each temperature, sixteen different kinetic runs were made at 10.37°, fifty-eight separate runs at 20.34°, and twenty runs at 29.67°. The individual first-order rate constants, k_{obs}, as well as the various iodide and hydrogen ion concentrations used are listed in Tables 15, 3, and 16. The summary of these temperature studies for the individual k_i values is given in Table 17.

Table 15. The Kinetic Data for the First Order Reaction of $HCrO_4^-$
at 10.37° and $\mu = 0.130$ M.

$10^2[H^+]$, M	$10^2[I^-]$, M	$10^4 k_{obs}$, sec^{-1}	$10^4 k_{calc}$, sec^{-1}
1.616	4.998	1.02	1.04
1.616	4.001	0.788	0.763
1.154	5.000	0.578	0.576
1.154	5.997	0.723	0.741
2.515	5.938	3.41	3.17
2.515	6.993	4.12	4.03
3.772	1.998	1.98	1.89
3.772	4.000	4.54	4.51
5.030	1.019	1.94	1.82
5.030	1.999	3.98	3.89
5.030	3.009	6.03	6.34
7.545	1.028	5.87	5.54
7.545	2.025	10.3	11.6
1.258	11.75	2.40	2.36
1.258	9.991	1.87	1.83
1.258	7.998	1.20	1.31

$[HCrO_4^-]_o = 1.5 - 2.0 \times 10^{-5}$ M

$S/X = 0.09$

$k_1 = 4.87 \times 10^{-2} \pm 7.0 \times 10^{-3}$ M^{-2} sec^{-1}

$k_2 = 63.5 \pm 7.4$ M^{-4} sec^{-1}

$k_3 = 108 \pm 3.8$ M^{-4} sec^{-1}

Table 16. The Kinetic Data for the First Order Reaction of $HCrO_4^-$
at 29.67° and μ = 0.130 M.

$10^2[H^+]$, M	$10^2[I^-]$, M	$10^4 k_{obs}$, sec^{-1}	$10^4 k_{calc}$, sec^{-1}
2.308	10.00	22.2	19.5
2.308	9.001	17.8	16.6
3.462	9.001	36.6	36.4
3.462	8.002	30.2	30.5
1.058	7.000	3.02	3.18
1.058	10.00	5.20	5.22
2.116	6.002	7.88	7.83
2.116	4.000	4.63	4.50
3.174	1.000	2.16	1.78
4.232	0.996	3.50	3.25
4.232	2.995	12.4	11.9
4.232	1.996	8.01	7.22
6.348	0.798	6.13	6.72
6.348	0.719	5.55	6.01
6.348	0.996	8.41	8.55
2.221	7.000	10.6	10.6
2.221	4.994	6.03	6.60
1.555	8.994	7.99	8.29
1.555	7.996	6.17	6.98
2.221	3.993	5.02	4.88

$[HCrO_4^-]_o$ = 1.5 - 2.0 × 10^{-5} M

S/X = 0.08

k_1 = 0.253 ± 0.032 M^{-2} sec^{-1}

k_2 = 201 ± 21 M^{-4} sec^{-1}

k_3 = 241 ± 15 M^{-4} sec^{-1}

Table 17. Temperature Dependence of the k_i Values in the Rate Law.

°C	k_1 M^{-2} sec^{-1}	k_2 M^{-4} sec^{-1}	k_3 M^{-4} sec^{-1}
10.37	0.0487 ± 0.007	63.5 ± 7.4	108 ± 4
20.34	0.206 ± 0.009	111 ± 7	154 ± 3
29.67	0.253 ± 0.032	201 ± 23	241 ± 15

The data from Table 17 can be used to determine the variation

of the rate constants, k_i, with temperature. From transition state

theory the relationship between the rate constant k_i and the tempera-

ture can be expressed as:

$$(58) \qquad \ln(k_i/T) = \ln(h/k) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT$$

where k_i is one of the three rate constants k_1, k_2 or k_3, and k is the

Boltzmann constant. A plot of $\log(k_i/T)$ versus $1/T$ should have a

slope that is equal to $-\Delta H^{\ddagger}/2.303R$ from which $\Delta H^{\ddagger}$ is obtained.

Figure 8 shows the result of this plot for the k_2 and k_3 terms. The

drawn lines are a visual fit of the points and are biased slightly in

favor of the 20.34° temperature result. This temperature point

represents the greatest number of kinetic runs made. The $\Delta S^{\ddagger}$

values were obtained from Equation (58) by chosing a value of k_i,

taking the $1/T$ reading from the graph for this value, and then using

the above calculated $\Delta H^{\ddagger}$. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the k_2 and k_3 terms
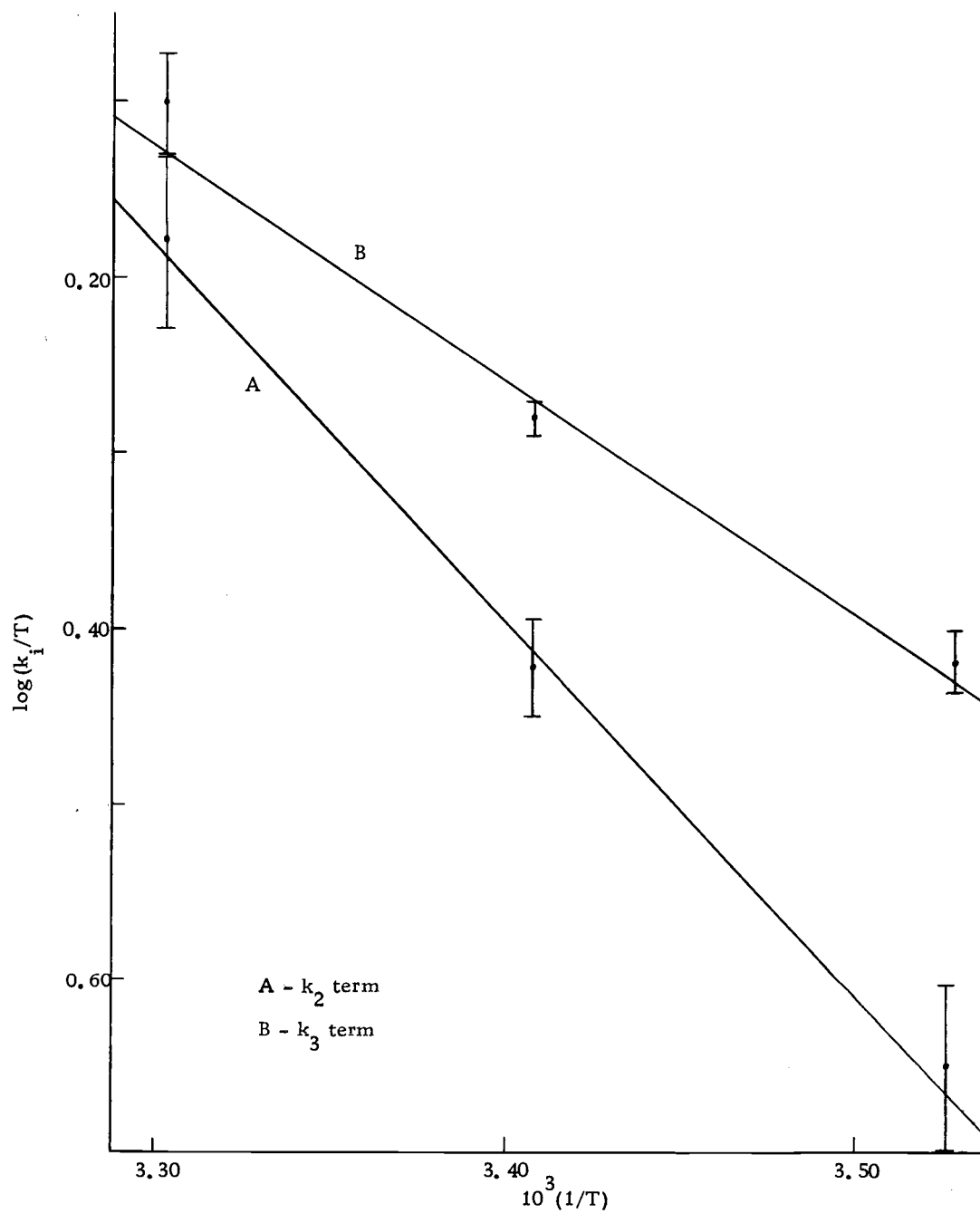
Figure 8. Temperature Dependence of the k_2 and k_3 Terms.

are listed in Table 18. The error values were determined by drawing

the maximum and minimum slopes through the error limits of the k_i

values. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined for each of these lines,

and the average deviation was used for the error limit.

Table 18. Summary of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the k_i Values.

Rate term	$\Delta H^{\ddagger}$, Kcal/mole	$\Delta S^{\ddagger}$, e.u.
k_1 (a)	----	----
k_2	9.6 ± 1.5	-16 ± 6
k_3	6.3 ± 1.0	-27 ± 3

(a) Values using k_1 from N_2-box runs were $\Delta H^{\ddagger}$ = 15 Kcal/mole and $\Delta S^{\ddagger}$ = -10 e.u.

The k_1 term could not be determined from the data since the

three points on the $\log(k_1/T)$ versus temperature plot were not linear.

No meaningful line could be drawn. If the N_2-box results are used

for another value of k_1, then at least an estimation of the $\Delta H_1^{\ddagger}$ and

$\Delta S_1^{\ddagger}$ can be made. The resulting values are: $\Delta H_1^{\ddagger}$ = 15 Kcal/mole

and $\Delta S_1^{\ddagger}$ = -10 e.u. These values are not compared directly with

the values for k_2 and k_3, since only the N_2-box value was used for the

k_1 term. Likewise, no error limits are given for the $\Delta H_1^{\ddagger}$ and

$\Delta S_1^{\ddagger}$. The values for k_1 should be considered as only approximate.

DISCUSSION

Mechanism

Rate Law

The kinetic study was made in the concentration region of chromate and acid in which $HCrO_4^-$ was the only major species. The H_2CrO_4 and $Cr_2O_7^{2-}$ could be neglected as chromate species. The reaction rate was followed under conditions in which first order dependence on $HCrO_4^-$ was observed. The dependencies of the hydrogen ion and iodide ion were determined by their effect on the pseudo-first-order rate constant.

The general rate law is formulated to be:

(59)   Rate = $[HCrO_4^-]$ $(k_1 [H^+][I^-] + k_2 [H^+]^2 [I^-]^2 + k_3 [H^+]^3 [I^-])$

Each term should represent an independent reaction pathway in which the hydrogen ions and iodide ions can add to the monohydrogen chromate species. There can be possible duplication of reaction steps in each of the three pathways, but each rate determining step must involve a different activated complex. Therefore, the reaction can be considered to have three mechanisms, and these will be developed in the following sections. While the proposed mechanisms are consistent with the rate law, they are not the only ones that can be postulated. However, the mechanisms can be judged by other chemical

data and the most reasonable ones can be chosen.

k_1-Term

The k_1-term represents the reaction mechanism in which there is first-order dependence for the iodide, hydrogen, and chromate ions. It can be represented by the following steps:

(60) $\qquad H^+ + HCrO_4^- \rightleftharpoons H_2CrO_4 \qquad 1/K_1 = 0.24 \ M^{-1}$

(61) $\qquad H_2CrO_4 + I^- \xrightarrow{k_a} \text{r. d. s.}$
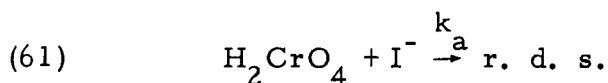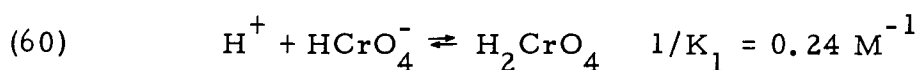
The first step is a pre-equilibrium protonation of the $HCrO_4^-$ to produce chromic acid, H_2CrO_4. The iodide ion then attacks the chromic acid in the rate determining step, r. d. s. The rate constant, k_a, can be obtained from the overall rate constant, k_1, and the $1/K_1$.

(62) $\qquad k_a = k_1 \cdot K_1 = 0.86 \ 1 \ mole^{-1} sec^{-1}$

The rate determining step may be pictured in two ways, either as a one electron or as a two electron transfer step. In a one electron step, the iodide could transfer its electron through a chromate oxygen.

(63) $\qquad (HO)_2OCr-O-I \rightarrow Cr(V) + I \cdot$
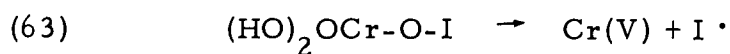
The resulting products would probably be a Cr(V) species and an iodine atom. In a two electron process the iodide would probably have to displace a water molecule from the chromate ion.

(64) $\qquad CrO_3 \cdot H_2O + I^- \rightleftharpoons ICrO_3^- + H_2O$
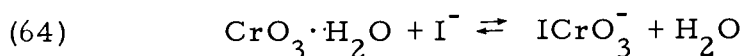
The species formed, $ICrO_3^-$, would then react in a rate determining process.

If the k_1-term is considered by itself, both pathways are possible. The formation of $ClCrO_3^-$ (30, 60) lends support to the latter process. However, in view of the overall rate law, the complex formation is more doubtful. If $ICrO_3^-$ can by itself produce a rate determining step, then an addition of either one proton or one iodide should provide another pathway. Terms which would indicate these pathways, $[H^+]^2[I^-]$ and $[H^+][I^-]^2$, were added to the rate law. The former value gave a rate constant that was considered undefined, 42% error limit. The latter term normally gave a rate law with a negative rate constant. Therefore, the reaction pathways with second order dependence in one of the ions and only first order dependence in the other ion are considered unlikely. The displacement of water by iodide in the k_1-term is not considered likely when the k_2-term is taken into account.

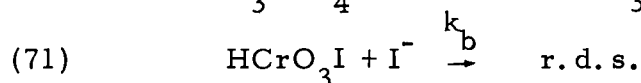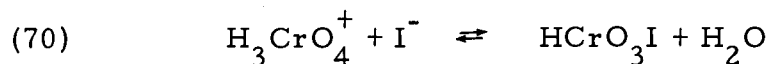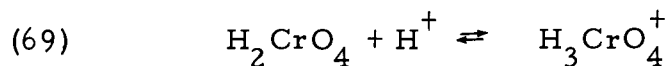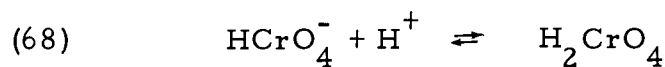There is one additional two electron process which could take place.

(65) $\qquad HOCrO^- + I^- \rightleftharpoons HOCrOI^{2-} \qquad K_a'$

(66) $\qquad HOCrOI^{2-} + H^+ \xrightarrow{\ k_a'\ } \qquad r.d.s.$
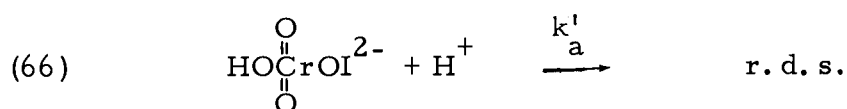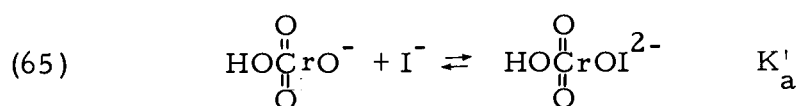
For this process the equilibrium constant K_a is unknown and k_a' cannot be determined. The last step can be represented as:

(67) $\qquad (HO)O_2Cr \cdot O \overset{\overset{+}{H}}{\underset{I}{\diagdown}} \quad \rightharpoonup \quad Cr(IV) + HOI$
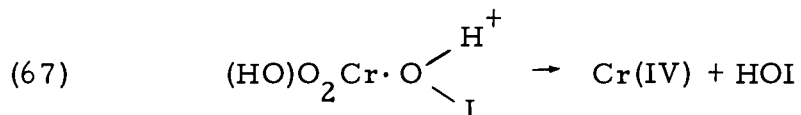
The only distinguishing feature between this mechanism and the previous one-electron mechanism is the first equilibrium step. The formation of chromic acid, Step (60), is a known reaction with a measured equilibrium constant. The first step, (65), in the latter mechanism has not been determined independently. However, there is no evidence for a definite choice between these two mechanisms. The one electron process seems more probable since the first step is a known equilibrium.

$\underline{k_2\text{-Term}}$

The mechanism associated with the k_2-term is more complex and has more possible reaction steps than the k_1-term. The hydrogen ion and iodide ion dependencies both have jumped to two in this step, and the mechanism has to show how these are involved. The following steps represent the mechanism proposed:

(68) $\qquad HCrO_4^- + H^+ \rightleftarrows H_2CrO_4$

(69) $\qquad H_2CrO_4 + H^+ \rightleftarrows H_3CrO_4^+$

(70) $\qquad H_3CrO_4^+ + I^- \rightleftarrows HCrO_3I + H_2O$

(71) $\qquad HCrO_3I + I^- \overset{k_b}{\rightarrow} \quad r.d.s.$

The first step is the same pre-equilibrium step suggested for the

k_1-term. The addition of another proton to chromic acid can give

the $H_3CrO_4^+$ from which iodide can displace a molecule of water. The

resulting species, $HCrO_3I$, is then attacked by a second iodide ion in

the slow step, (71). All steps previous to the rate determining step

are shown as equilibrium reactions, but they have not been evaluated

as such. Therefore, the value of k_b cannot be obtained from the

over-all rate constant k_2. The activated complex for this mechan-

ism is postulated as being $HCrO_3I_2^- \cdot xH_2O^{\ddagger}$.

There are other possibilities for this reaction pathway. Steps

(69) and (70) could be interchanged as:

(72) $\qquad H_2CrO_4 + I^- \rightleftharpoons CrO_3I^- + H_2O$

(73) $\qquad CrO_3I^- + H^+ \rightleftharpoons HCrO_3I$
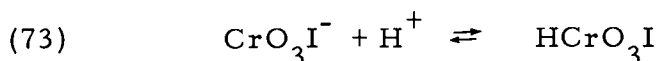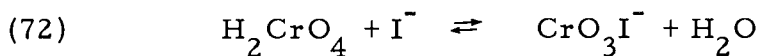
The same slow step, (71), is retained in this scheme as well as the

same form of the activated complex. This mechanism has an ana-

logue in the formation of the chromate-phosphate complex discussed

in the introduction. The choice between this mechanism and the

previous one is whether the proton adds before or after the iodide

ion displaces water. There is no way to distinguish between Steps
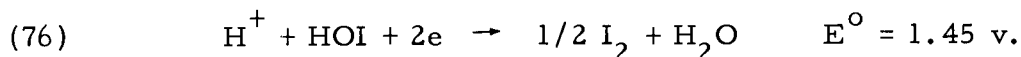
(69)-(70) and Steps (72)-(73) with the present data.

Since there are two iodides in the k_2-step, there are four pos-

sibilities for the number of electrons transferred in the activated

complex. In a one electron transfer step the second iodide ion would most likely be attached to the already present first iodide. It is difficult to see why two iodides would be required for the transfer of only one electron so the one electron step can be considered unlikely in the k_2-term.

A four electron transfer would probably result in a step:

(74) $$HCrO_3I_2^{-\ddagger} \rightarrow Cr(II) + 2HOI$$
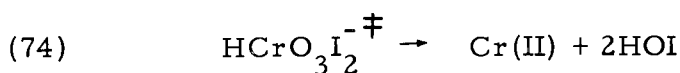
The production of Cr(II) using iodide ion as the reducing agent is not likely. The oxidation potentials which would be involved in this reaction are shown with the Cr(IV)-Cr(II) couple estimated from the values listed on page 14.

(75) $\quad\quad$ $Cr(IV) + 2e \rightarrow Cr(II)$ $\quad\quad\quad$ $E^o = 0.67$ v.

(76) $\quad\quad$ $H^+ + HOI + 2e \rightarrow 1/2\ I_2 + H_2O$ $\quad\quad$ $E^o = 1.45$ v.

If the production of Cr(II) results from a four electron transfer, the system, for simplification, can be pictured as going from $Cr(VI) \rightarrow Cr(IV) \rightarrow Cr(II)$. From the E^o values the last step has an estimated free energy change of +36 Kcal/mole. This energy barrier does not favor the production of Cr(II) if iodide ion is used as the reducing agent. This step will not be considered further.

With the one and four electron steps removed from consideration, the two and three electron transfers can be considered in more detail. A two electron step has been established in chromate

reductions (28, 47, 66, and 69) when the reducing agents can lose

two electrons. A three electron step has been suggested by Haight

(31) in the oxidation of S(IV), but it is limited to this example at the

present.

The two electron transfer may be represented as having the

following step:

$$\text{(77)} \qquad \text{HCrO}_3\text{I}_2^{-\ddagger} \rightarrow \quad \text{Cr(IV)} + \text{I}_2$$
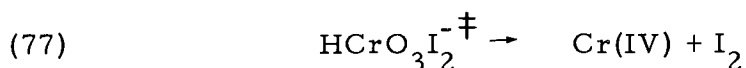
This representation implies that the second iodide ion is bound to the

already present iodide. This formulation has the advantage of yield-

ing one stable leaving group, the I_2, and only one high energy inter-

mediate, Cr(IV).

For formation of I_2 in the rate determining step has been sup-

ported by Howlett's (36) study. He found that iodine retarded the

reaction. The interpretation of this effect is that the reaction

$$\text{(78)} \qquad \text{Complex} + \text{I}^- \rightleftharpoons \quad \text{Cr(IV)} + \text{I}_2 \qquad \text{r.d.s.}$$
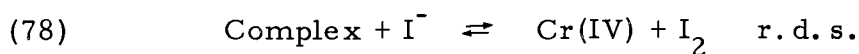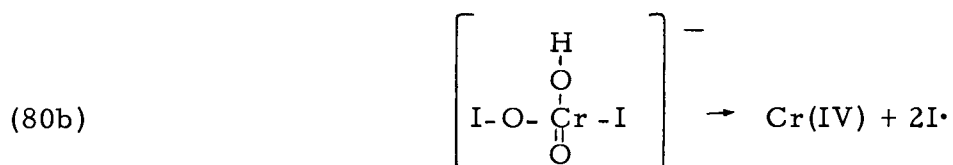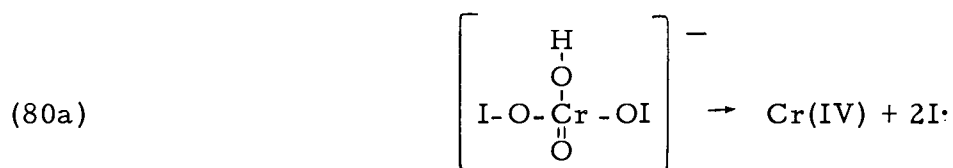
is reversible. The implied activated complex for this pathway

would be a species in which an iodine-iodine bond is formed. This

reversible slow step was used to explain the data in Howlett's study.

In other probable two electron steps, the possible sites for

reaction by the second iodide ion would be on a bound oxygen or on a

displacement of OH^- to give a complex:

(79)

$$\left[\begin{array}{c} H \\ | \\ O \\ | \\ I\text{-}\overset{|}{\underset{\|}{C}r}\text{-}I \\ O \end{array}\right]^{-}$$
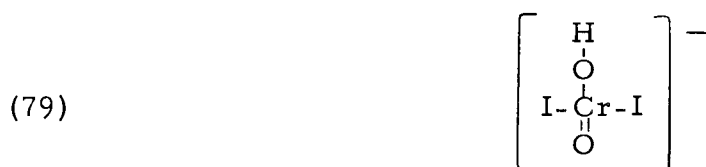
The latter possibility has the undesirable feature of an iodide ion displacing a hydroxide ion from the chromate. Normally a water molecule is postulated to be the leaving group in a displacement of this type. The former possibility would produce either a complex such as (80a) or (80b).

(80a)

$$\left[\begin{array}{c} H \\ | \\ O \\ | \\ I\text{-}O\text{-}\overset{|}{\underset{\|}{C}r}\text{-}OI \\ O \end{array}\right]^{-} \rightarrow Cr(IV) + 2I\cdot$$

(80b)

$$\left[\begin{array}{c} H \\ | \\ O \\ | \\ I\text{-}O\text{-}\overset{|}{\underset{\|}{C}r}\text{-}I \\ O \end{array}\right]^{-} \rightarrow Cr(IV) + 2I\cdot$$

In either case, if only one electron is transferred by each iodide ion, three unstable species are produced. No stable compound would be produced. The complex (80b) would probably not have a two electron step. The iodide ion bound to the chromium could lose two electrons while the iodide ion bound to oxygen could lose one electron. This type of complex could give a three electron transfer which will be discussed next.

A three electron transfer has been suggested for the S(IV)-Cr(VI) reaction in which a chromate complex with two SO_3^{2-} can form. In the chromate-iodide reaction the activated complex can have one of
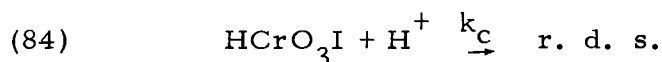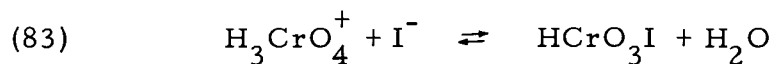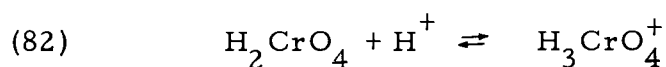
the structures presented in Equations (77), (79), (80a), and (80b). If the second iodide ion adds to the first one which is already bound to the chromate, Equation (77), a three electron step appears to be unlikely. Instead of producing the stable I_2 and one unstable Cr(IV), a three electron process would produce the stable Cr(III) and two unstable species, I· and HOI. The second activated complex presented in Equation (79) would probably have a three electron step. There is no easy way for iodine to form, and the stable Cr(III) could be produced. However, as stated earlier, the second iodide would have to displace a hydroxide group from the chromate ion, and this does not appear to be likely. The third activated complex, Equation (80b), can also produce a three electron step with the formation of Cr(III), I· and HOI. Again iodine cannot be formed easily and could not account for the retardation found in Howlett's study. There appear to be no other independent points against this last structure.

These two types of reactions, a two and a three electron process, are possible with the activated complex $HCrO_3I_2^- \cdot xH_2O^{\ddagger}$. The discussion above indicates that a two electron step is preferable. The study by Howlett was explained by the reversible reaction of iodine with Cr(IV). There is only one high energy intermediate produced in the two electron step, but at least two high energy species are produced if a three electron step is taken. The studies of other redox systems have also shown the two electron step to be the

most common (28, 47, 66 and 69). The main difference in the two

schemes is whether Cr(IV) or Cr(III) is produced from the activated

complex. The direct production of Cr(III) would exclude the

Westheimer mechanism for this system. The formation of Cr(IV)

leads to a possibility of the Westheimer mechanism, and further spec-

ulation about its reactions can give a better understanding of the

mechanism. The two electron step will therefore be considered to

be the step occurring in this reaction pathway.

k_3-Term

The pathway for the k_3-term can be considered to be similar to

that for the k_2-term.

$$(81) \qquad H^+ + HCrO_4^- \rightleftharpoons H_2CrO_4$$

$$(82) \qquad H_2CrO_4 + H^+ \rightleftharpoons H_3CrO_4^+$$

$$(83) \qquad H_3CrO_4^+ + I^- \rightleftharpoons HCrO_3I + H_2O$$

$$(84) \qquad HCrO_3I + H^+ \xrightarrow{k_c} \quad r.\ d.\ s.$$

The difference between the k_2-term and the k_3-term pathways is the

reaction of the $HCrO_3I$ species. In Step (84) another proton adds to

this complex to form an activated complex, $H_2CrO_3I^+ \cdot xH_2O^\ddagger$. It

contains one more hydrogen ion and one less iodide than the activated

complex for the k_2-term. Again, none of the pre-equilibrium terms

have been determined and the actual value of k_c cannot be obtained

from the overall constant k_3. The other possible combinations of

Steps (81), (82), and (83) have been discussed in the previous two

sections.

What occurs after the rate determining step in this pathway is

only speculation. Probably the addition of the proton only gets the

complex over the energy barrier. The complex may have a fast re-

action with a second iodide ion. This mechanism would give the pos-

sible electron transfers discussed in the k_2-term. If only the single

iodide took part in the reaction, it would probably give a two electron

transfer step.

$$(85) \qquad \begin{array}{c} H \\ | \\ O \\ | \\ H\text{-}O\text{-}Cr \text{---} I \\ || \\ O \end{array} \rightarrow Cr(IV) + HOI$$
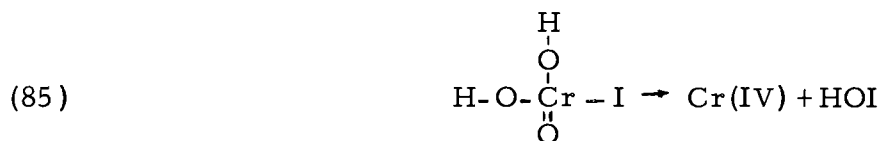
With the present information a choice cannot be made for the mechan-

ism. For either choice, a k_2-term step with an added proton or a

single iodide reaction, $Cr(IV)$ is again assumed to be a produce from

the activated complex.

Chromium Intermediates

The chromium (VI) must pass through the oxidation states of

+5 and +4 before it becomes the stable $Cr(III)$ ion. As discussed in

the introduction, these intermediate chromium species have been

indicated by induced reactions observed in many chromate reductions.

There is a possibility that a chromium intermediate is produced in this system. The production of Cr(IV) is quite possible in all three pathways, and Cr(V) could be produced in the k_1-term. Consequently, the reactions of the chromium intermediates can be important in the mechanism.

In order to account for the induction factor, 2.0, of the iodide ion in chromate reductions, the following reaction of Cr(V) is assumed:

(86) $Cr(V) + I^- \rightarrow Cr(III) + HOI$ (24, 67)

This reaction is presumed to be faster than the reaction of Cr(V) with other reducing agents. Therefore, when iodide ions are added to the chromate reactions, the iodide removes the Cr(V) from further reactions. The iodide loses two electrons for every Cr(V) produced, but the other reducing agent loses only one electron in reducing Cr(VI) to Cr(V). See the introduction for further discussion.

The other reaction with Cr(V) and iodide would be a one electron step such as Espenson and King (24, 25) found for the Cr(V) reaction with Fe(II) and V(IV).

(87) $Cr(V) + I^- \rightarrow Cr(IV) + I\cdot$

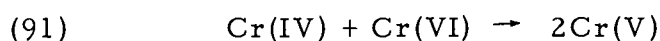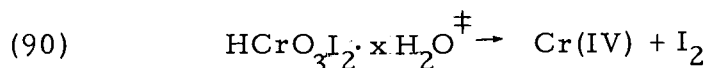(88) $Cr(V) + Fe(II) \rightarrow Cr(IV) + Fe(III)$
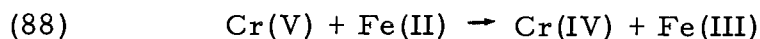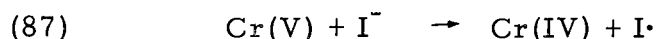
This reaction produces two high energy species for each unstable Cr(V) that reacts. Westheimer (67) believed this possibility was

unlikely. To account for the induction factor, the reaction

(89) $\qquad Cr(IV) + I^- \rightarrow Cr(III) + I \cdot$
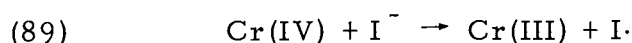
must also be rapid. This scheme leads to an inconsistency if the

initial reactant has a two electron transfer step, (18). The Cr(IV)

produced should react rapidly with iodide instead of Cr(VI), and the

induction factor would then be 0.5 instead of 2.0. Therefore, it is

assumed that the major pathway of reaction for Cr(V) is Equation (87)

and not Equation (89). It cannot be stated that Reaction (89) does not
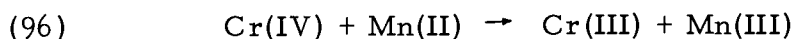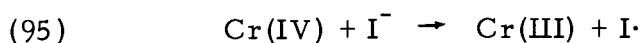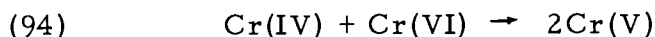
take place at all, but it can be only a minor pathway.

The Cr(IV) species has more possible reactions, and

Westheimer's (67) discussion of these has been presented in the intro-

duction. In the following discussion the k_2 activated complex is used

to illustrate the possible reactions after the rate determining step.

This step is used since it is representative of the other steps, and it

illustrates most of the reactions. In the Westheimer mechanism the

k_2 step would proceed:

(90) $\qquad HCrO_3I_2 \cdot x H_2O^{\ddagger} \rightarrow Cr(IV) + I_2$

(91) $\qquad Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$

(92) $\qquad Cr(V) + I^- \rightarrow Cr(III) + HOI$

(93) $\qquad H^+ + HOI + I^- \rightarrow H_2O + I_2$

Again the principal feature of this mechanism is the rapid reaction of

Cr(IV) with Cr(VI) rather than with I^-. The Mn(II) ion has been

shown to compete with the Cr(VI) anion for the Cr(IV) intermediate.

The Mn(II) can thereby diminish the rate at which the Cr(VI) disappears in the reaction and can decrease the reaction rate by one-half.

The results of this kinetic study show that the Mn(II) ion does not affect the reaction rate and does not even reduce the amount of triiodide produced. The three possible reactions of Cr(IV) are:

(94) $Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$

(95) $Cr(IV) + I^- \rightarrow Cr(III) + I\cdot$

(96) $Cr(IV) + Mn(II) \rightarrow Cr(III) + Mn(III)$

These steps include the Westheimer-proposed reaction plus the additional Step (95) for this particular system. Reaction (96) is known to compete for the Cr(IV) over Reaction (94). Therefore, a Cr(VI) reaction pathway is blocked, and the reaction rate is retarded. Since the rate of reaction was not retarded with the addition of Mn(II), the Westheimer steps cannot explain our observations. However, if Step (95) takes place and is a major reaction pathway, then the effect of Mn(II) can be explained. The further reaction of I· in Step (95) will be discussed in the next section and its presence only indicated here. Reaction (95) does not involve Cr(VI) and so any competing chemical pathway will not necessarily influence the rate of the reaction. With added Mn(II) Step (96) can compete with Step (95) to form Mn(III) and Cr(III). It has been shown in this study that Mn(III) reacts rapidly with iodide ion in acid solution. Its reactions is

suggested to be:

(97) $Mn(III) + I^- \rightarrow Mn(II) + I\cdot$
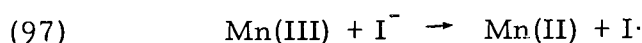
If Step (96) does compete with Step (95), further reaction of the

Mn(III), as in Step (97), will have no net effect in the reaction solu-

tion. One Cr(III) and one I· will be produced for every one Cr(IV).

At the end of the reaction the Mn(II) will still be in the same oxida-

tion state whether it does or does not react with Cr(IV). There

would be no oxidizing power loss, no change in the rate of reaction,

and no change in the deviation from first order plots. These obser-

vations have been noted in the experiments with added Mn(II) ion.

Therefore, either chromium (IV) is not produced in the reaction

(this appears to be unlikely) or the iodide ion competes for the Cr(IV)

over the Cr(VI). Either way, the Westheimer mechanism does not

appear to be operative in this kinetic study.

By using thermodynamic calculations based on the estimated

E^o values which were calculated in the introduction, the reaction of

Cr(IV) with iodide was expected. The free energy of the reaction

(98) $2Cr(IV) + 2I^- \rightarrow 2Cr(III) + I_2$
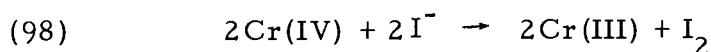
is -55 Kcal/mole if the E^o for the Cr(IV)-Cr(III) couple is equal to

1.73 v. If the potential of 2.01 v. estimated by Csanyi (14) is used,

the free energy change is even greater. The reaction is predicted

to occur with either value. The rate at which it occurs cannot be

determined by thermodynamics, and no kinetic studies of this

particular reaction have been made. The studies by Espenson, King,
and Tong (24, 25 and 61) have shown that normally the coordination
change, $Cr(V) \rightarrow Cr(IV)$, is the slow reaction, and that by compari-
son the $Cr(IV) \rightarrow Cr(III)$ is rapid. Reaction (98) would be expected
to be rapid. Westheimer's mechanism does not allow this reaction
to compete with the $Cr(VI) + Cr(IV)$ reaction. However, his mechan-
ism has only been tested under conditions where $[I^-]/[HCrO_4^-] \sim 10$.
Under these conditions the $Cr(IV)$ may be selective enough to react
almost exclusively with $Cr(VI)$. In our kinetic study the
$[I^-]/[HCrO_4^-]_o$ is greater than 1,500 in the $Mn(II)$ experiments, and
the $Cr(IV)$ probably reacts with the higher concentration of iodide ion.
Westheimer's mechanism may hold under the former conditions, but
may not under our conditions.

In the present study, no effect was noticed when an initial con-
centration of iodine, $[I_2]_o/[HCrO_4^-]_o = 5.7$, was placed in the solution.
This observation is in contrast to the retarding effect which Howlett
(36) attributed to iodine. He interpreted the rate determining step
to be reversible:

(99) $\qquad Cr(VI) \cdot 2I^{\ddagger} \rightleftharpoons Cr(IV) + I_2$
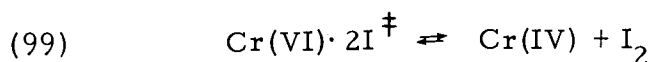
This step, (99), allows for another possible reaction for $Cr(IV)$ in
addition to those stated earlier, Steps (94), (95), and (96). Howlett
has used the Westheimer mechanism, neglecting Reaction (95), to
account for the kinetics observed. He proposed the rate law:

(100)   Rate = $\dfrac{k[Cr(VI)]^2[I^-]^2[H^+]^2}{k'[I_2] + k''[Cr(VI)]}$

Howlett found the ratio k''/k' to be equal to 0.10. This implies that

I_2 should react with Cr(IV) more rapidly than does Cr(VI). In our

experiment the iodine should have made the reaction tend toward

second order in Cr(VI) since $k'[I_2] > k''[Cr(VI)]$. This rate law is

not in accord with our observations. If the reaction, $Cr(IV) + I^- \rightarrow$

$Cr(III) + I\cdot$, Step (95), is included in Howlett's scheme, then both

his results and ours can be accommodated. The iodide ion can com-

pete for the Cr(IV); therefore, the iodine will no longer be able to

reverse the reaction. The concentration of Cr(VI) in Howlett's study

was 100 times greater than ours, and therefore his ratio,

$[I^-]/\Sigma[Cr(VI)]$, is between 1.0 - 10. The Westheimer mechanism

could be operative under these conditions. With the $[I^-]/\Sigma[Cr(VI]$

equal to 1.5×10^3 in our study, again the evidence supports Reaction

(95) and not the Westheimer mechanism.

Only an approximate ratio of the reactivity of I_2 and Cr(VI)

for Cr(IV) was given in Howlett's paper. Therefore, only the above

qualitative argument can be used for the difference observed in the

I_2 behavior. The statement in Howlett's paper (36, p. 686) that

"Cr^4 is not a strong oxidizing agent" is not correct. His statement

should have been that the Cr(IV)-Cr(VI) couple may be low enough

for iodine to oxidize the Cr(IV) to Cr(VI). The E^o value predicted

for the Cr(IV) → Cr(III) reaction is greater than 1.61. This species must be regarded as a strong oxidizing agent. In all calculations for the E^o values the acid dependencies of these reactions have been omitted. Therefore, any detailed calculations, such as equilibrium constants, using these values would not be very useful. It can be said that Cr(IV) is a strong oxidizing agent, but it can also be oxidized to Cr(VI).

Iodine Intermediates

The production of HOI as an iodine intermediate has been proposed in the reaction of Cr(V) with iodide.

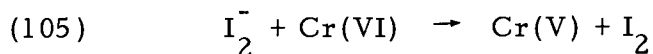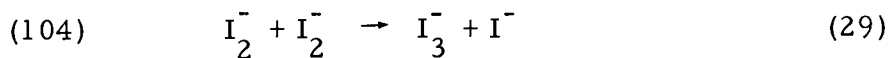(101) $\qquad$ Cr(V) + I⁻ → Cr(III) + HOI
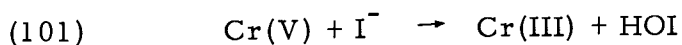
Westheimer (67) has discussed this reaction. Since Cr(V) can be present as an intermediate in this reaction, the further reaction of HOI must be considered. It is known that HOI reacts rapidly with I⁻ in acid solution (49).

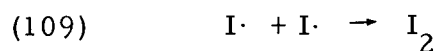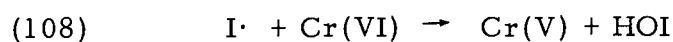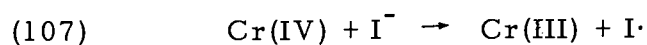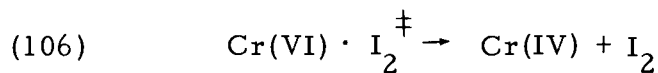(102) $\qquad$ $HOI + I^- + H^+ \rightarrow H_2O + I_2$
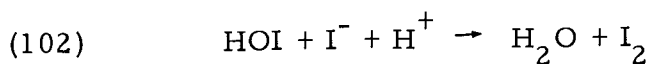
HOI is therefore removed as a reaction product and considered to no longer influence the reaction.

The production of iodine atoms in the reaction is a likely possibility, and reactions involving the intermediate, I·, must be considered. The reactions for this species are:

(103) $\qquad$ $I\cdot + I^- \rightleftharpoons I_2^-$ $\qquad$ (5, 12, 29)

(104) $\qquad$ $I_2^- + I_2^- \rightarrow I_3^- + I^-$ $\qquad$ (29)

(105) $\qquad$ $I_2^- + Cr(VI) \rightarrow Cr(V) + I_2$

Reaction (103) is the formation of diiodide ion. In an iodide solution the iodine atoms should be considered to be in this form (5, 12, 29). However, the I_2^- will be represented as $I\cdot$ in the mechanisms to aid in balancing the reaction steps and to keep the mechanisms from becoming cumbersome. Reaction (104) is the combination of diiodide ions to form a stable triiodide ion and is a terminating step for this intermediate. Step (105) leads to an alternative mechanism to the Westheimer mechanism.

(106) $\qquad$ $Cr(VI) \cdot I_2^{\ddagger} \rightarrow Cr(IV) + I_2$

(107) $\qquad$ $Cr(IV) + I^- \rightarrow Cr(III) + I\cdot$

(108) $\qquad$ $I\cdot + Cr(VI) \rightarrow Cr(V) + HOI$

(109) $\qquad$ $I\cdot + I\cdot \rightarrow I_2$

This mechanism is in general analogous to those postulated by Wilberg and Richardson (70) and by Roček (54) in other redox reactions with chromic acid. These have been discussed in the introduction under the heading "Alternative Mechanism". The distinguishing feature of this mechanism is that Step (109) is probably very rapid; therefore, Step (108) would have to compete for the $I\cdot$.

Step (108) provides a second reaction pathway for the Cr(VI). Without

this step and assuming the Westheimer mechanism to hold at high

Cr(VI) concentrations, the rate of reaction should begin to double at

some ratio of $[I^-]/[Cr(VI)]$. The kinetic run made with

$[HCrO_4^-]_o = 5.0 \times 10^{-4} M$ was slightly slower than a run with

$[HCrO_4^-]_o = 1.6 \times 10^{-5} M$. Either the initial Cr(VI) concentration was

still not high enough to detect this doubling in rate, or there are two

pathways in which the Cr(VI) can react in each mechanism. Mn(II)

ion would have no effect upon this mechanism since its reaction with

Cr(IV) would not produce any net effect upon the concentration of $I\cdot$

Deviation from First-Order Kinetics

Zero-Order Term

The deviation from first order kinetics for $HCrO_4^-$ is toward a

lower order, such as zero. If a zero-order term in $HCrO_4^-$ is added

to the first-order term, the rate equation becomes:

$$(110) \qquad \frac{-d[HCrO_4^-]}{dt} = k_1[HCrO_4^-] + k_o$$

As long as $k_1[HCrO_4^-] \gg k_o$, first-order kinetics are followed. If

$k_1[HCrO_4^-] \gg k_o$, then a reaction order of less than one is predicted

for $HCrO_4^-$. The behavior of the kinetic runs in our study follows

the latter condition. At high initial chromate concentrations,

first-order dependence was found for the first two half-lives.   After

this period, a deviation began to appear toward a lower order in

$HCrO_4^-$.   However, at low initial chromates the first-order plots

were curved in the first half-life.   If Equation (110) is integrated,

the expression

$$(111) \qquad \ln\left[1 + \frac{k_1[HCrO_4^-]}{k_o}\right] - \ln\left[1 + \frac{k_1[HCrO_4^-]_o}{k_o}\right] = -k_1 t$$

is obtained.   Since $\ln(1 + k_1[HCrO_4^-]_o/k_o)$ is a constant, a graphical

plot of $\ln(1 + k_1[HCrO_4^-]/k_o)$ versus $k_1 t/2.303$ should result in a

straight line with a slope equal to -1.00.   The k_1 value can be obtained

from the straight portion of the first-order plots.

The value of k_o is not known but can be determined indirectly.

Using a standard kinetic run various values were tried for k_o until

a line with a slope equal to -1.00 was obtained.   The kinetic run used

for this trial was made in the vacuum-line condition listed in Table 3,

$[H^+] = 0.02233$, $[I^-] = 0.060$ M, and $[HCrO_4^-]_o = 1.65 \times 10^{-5}$M.

A k_o equal to 1.3×10^{-10}M sec^{-1} was obtained from this trial.   This

k_o value was used to produce plots for other kinetic runs made in the

same series, Table 3 type 3.   The plots were linear with slopes close

to -1.0, and a typical plot for the data using this calculation is shown

in Figure 9.   The slopes of the plots are recorded in Table 19.

Table 19 also contains the percent of the reaction completed, the

initial concentration of $HCrO_4^-$ and the percent of the initial reaction
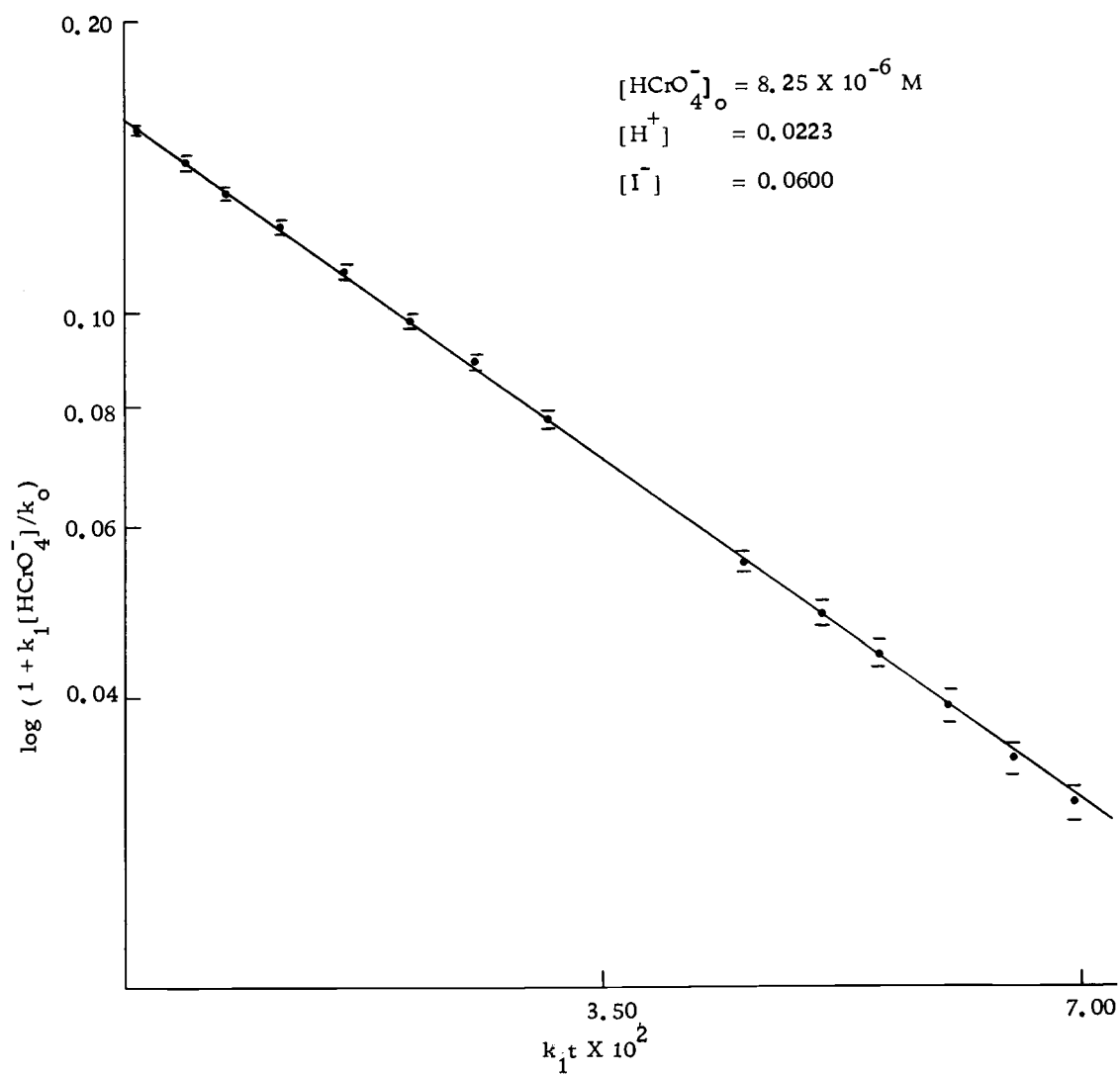
Figure 9. Plot of log $(1 + k_1[HCrO_4^-]/k_o)$ versus $k_1 t$.

that proceeds by the k_o term. The percent of reaction completed

refers to the length of time the kinetic run was followed. The rate

expression $k_1[HCrO_4^-] + k_o$ accounted for the data over this time

period. The zero-order term can account for the rate of reaction

observed, but this fit may only be superficial. It does not necessarily

imply a separate pathway of reaction.

Table 19. The Percent of Initial Reaction Proceeding by a
Zero-Order Term.

	$10^5 [HCrO_4^-]_o$ M	% Reaction Completed	Slope	Value of $10^9 k_1 [HCrO_4^-]_o$ M sec^{-1}	$\dfrac{k_o}{k_1[HCrO_4^-]_o} \times 100$ [a]
b	1.65	97.3	-0.965	3.87	3.4
	2.47	82.7	-1.00	5.74	2.3
	0.825	86.3	-1.02	1.91	6.8
	0.495	88.6	-0.975	1.10	11.8

$[I^-]_o = 0.0600$ M, $[H^+]_o = 0.0233$ M

a Percent of initial reaction proceeding by a zero-order term.

b Run used to obtain value of $k_o = 1.3 \times 10^{-10}$ M sec^{-1}

Chain Mechanism

The deviation from first-order kinetics could be the result of

a chain reaction involving radicals. If only one-electron steps are

used for the reduction of the chromium intermediates, Cr(V) and

Cr(VI), the following mechanism could result:

(112) $\qquad$ $Cr(VI) + 2I^- \rightarrow Cr(IV) + I_2$

(113) $\qquad$ $Cr(IV) + I^- \rightarrow Cr(III) + I\cdot$

(114) $\qquad$ $I\cdot + Cr(VI) \rightarrow Cr(V) + HOI$

(115) $\qquad$ $Cr(V) + I^- \rightarrow Cr(IV) + I\cdot$

(116) $\qquad$ $I\cdot + I\cdot \rightarrow I_2$
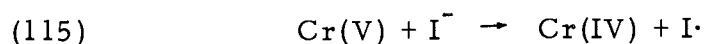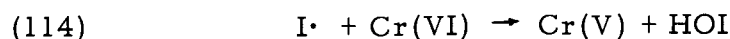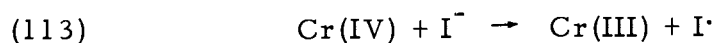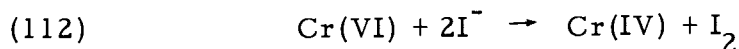
For every $I\cdot$ reaction with Cr(VI), Step (114), two more $I\cdot$'s may be produced by the follow-up steps, 115 and 113. A branching mechanism could result and soon become the predominant reaction. However, the combination of two iodine atoms to form a molecule, chain breaking Step (116), is probably more efficient than Step (114). The combination of iodine atoms does not allow the chain to grow. A steady state approximation for this mechanism does not yield a simple solution. The resulting equation is quadratic in the concentration of $I\cdot$. This equation cannot be solved without assumptions for the rates of the various steps. These assumptions are not justified with the present knowledge.

Other steps may be included in the chain mechanism, such as:

(117) $\qquad$ $Cr(V) + I^- \rightarrow Cr(III) + HOI$
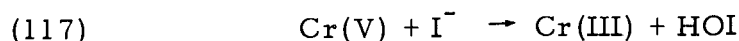
This step would allow for a second reduction pathway for Cr.(V), and could reduce the radical production by Step (115). The chain mechanism could depend on the relative rates of these two reactions. If Step (115) does proceed, the order of the reaction in $HCrO_4^-$ could

be less than one. The controlling steps for the chain mechanism can be the termination, Step (116), and Step (117).

The key experimental results for interpreting the downcurvature are: (1) the deviation from first-order was noticed in vacuum line runs indicating that oxygen was not causing the curvature, (2) the initial concentration of iodine did not affect the rate of reaction, (3) the wave length and measuring light did not appear to affect the reaction, and (4) the theoretical amount of triiodide ion was obtained. These observations indicate that the deviation is due to the main reaction. The iodine is probably not the source of the radicals since an increase in its concentration did not cause additional curvature. If there were a process by which $I\cdot$ could be produced independent of the chromate and iodine source, the observed deviation could be explained. Since there is no apparent method to produce $I\cdot$ independently in the reaction, the chain mechanism has been postulated.

The deviation from first-order was always noticed in the runs, but it was in the second to third half-life that the points contained large error limits. The previous derivation which involved a zero-order term as well as the first-order term could account for the data observed. However, this correction for zero kinetics was not precise enough to warrant correcting the k_{obs} which was obtained from the initial portion of the curve. A correction of this type would rely on the best fit of points that have large error limits. The k_{obs}

values are felt to be more accurate without this correction.

An effective scavenger for the I_2^- could not be found for this system. If I_2^- could be trapped or removed efficiently as I_2, the deviation from first-order kinetics should disappear. The added scavenger cannot react directly with the reactants or products. This condition limits the choice. The normal radical scavengers react with iodine to produce $I\cdot$ (63), but the opposite reaction is needed. The search was not successful. Allylacetate was added to see if it would interfere with the radical process (8, 11, and 26). However, it appeared to cause an increase in the rate of the $HCrO_4^-$-iodide reaction and did not appear to affect the curvature in the first-order rate plots. Its influence in the reaction was probably other than as a reactant for the intermediates. According to Boyer and Ramsey (11), the conversion of $I\cdot$ to I_2^- should decrease the inter-action of the iodine atom with double bonds. Therefore, the allylace-tate probably should not be expected to react with the iodine inter-mediate I_2^-.
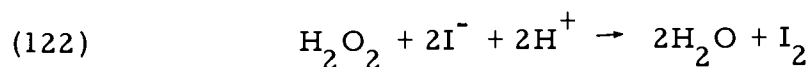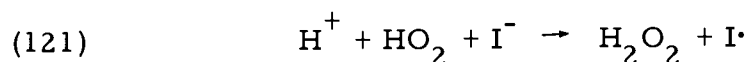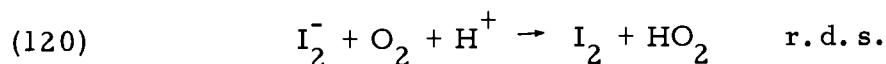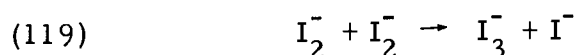
Oxygen Effect

The presence of the diiodide ion is implicated by the effect of oxygen upon the reaction. Boyer and Ramsey (11) have reported that systems in which I_2^- is an intermediate catalyze the reaction between oxygen and iodine. The studies have also shown that this catalytic

process is more pronounced at higher acid concentrations, normally 0.01 M and higher.

Excess triiodide ion is produced when oxygen is added to the chromate-iodide system. This excess iodine could not be accounted for by the combination of the initial concentration of chromate and the additional triiodide produced in the blank run without chromate ion. The chromate-iodide reaction probably forms an intermediate which catalyzes the iodide-oxygen reaction.

In other studies it has not been postulated that oxygen reacts with the intermediates, $Cr(IV)$ and $Cr(V)$. Oxygen can react with $Cr(II)$, but as shown earlier, the production of $Cr(II)$ is not likely in this system. Since I_2^- is probably present and is postulated as being a catalyst for the O_2-I^- reaction, it is most likely the species responsible for the catalysis in this study.

The following steps have been suggested for this catalysis (11).

(118) $$I\cdot + I^- \rightarrow I_2^-$$

(119) $$I_2^- + I_2^- \rightarrow I_3^- + I^-$$

(120) $$I_2^- + O_2 + H^+ \rightarrow I_2 + HO_2 \qquad r.d.s.$$

(121) $$H^+ + HO_2 + I^- \rightarrow H_2O_2 + I\cdot$$

(122) $$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$$

For every I_2^- that reacts with O_2 in Step (120), another I_2^- is produced in Step (121). The oxygen reaction causes no net change in

the system except that excess triiodide ion is produced.

Boyer and Ramsey (11) have reported Step (120) to be the rate determining step. Their assumption was based on increased catalytic behavior as the acid concentration was increased. In our study the O_2-I^- reaction does not produce much excess triiodide because of the relatively low acid concentration, 0.1 M or less. At the highest oxygen condition only 23% excess triiodide ion is produced. In normal N_2-flush runs the excess was less than 3% of the total produced. Therefore, no kinetic effect was noticed from this reaction in the N_2-flush runs.

The presence of diiodide ion is indicated by the catalysis of the oxygen-iodide reaction. This reaction should have no influence on the rate of the chromate-iodide reaction. The catalysis is not efficient due to the low acid concentration in our study, and therefore the production of the triiodide is not noticed in the rate of reaction. For every I_2^- that reacts with oxygen, one is given back with no net change in the number of intermediate particles.

Effect of Added Anions

The addition of chloride and bromide ions did not result in any change in the kinetics of the reaction. The reaction of chromate with chloride has been mentioned in the introduction, and the species

$ClCrO_3^-$ should have some effect on the chromate-iodide reaction.

(123) $\quad H^+ + HCrO_4^- + Cl^- \rightleftharpoons ClCrO_3^- + H_2O \quad K = 11 \ M^{-2}$
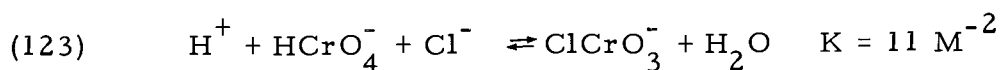
The concentration of $ClCrO_3^-$ should have been ten percent of the total

chromate concentration at the highest Cl^- concentration used.

There can be two reasons that the chloride ion does not affect

the reaction. The first is that iodide ion finds no difference in the

leaving ability of Cl^- and H_2O from the chromate ion.
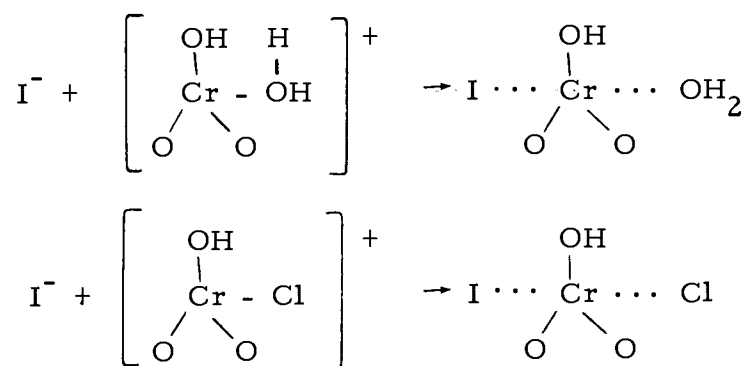
The other explanation is that in both cases the leaving group is H_2O.

Thus the formation of the iodochromate complex could be:
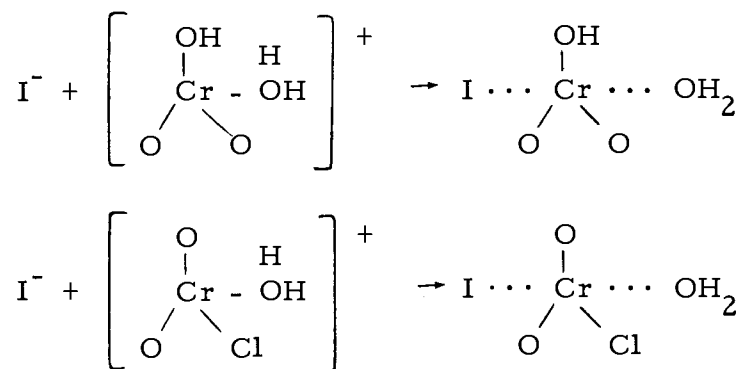
When a Cl^- rather than an hydroxide is bound to chromium, there

is not enough difference in the electron density around the central

chromium to effect the approaching iodide ion. Either explanation

fits the results. However, it remains that nothing can be said about

the relative reactivity of the halogens toward the chromate ion.

BIBLIOGRAPHY

1. Ardon, Michael and Gabriel Stein. The oxidation of chromous perchlorate solutions by molecular oxygen. Journal of the Chemical Society, 1956, p. 2095-2097.

2. Arley, Niels and K. Rander Buch. Introduction to the theory of probability and statistics. New York, John Wiley and Sons, 1950. 236 p.

3. Awtrey, Alice D. and R. E. Connick. The absorption spectra of I_2, I_3^-, I^-, IO_3^-, $S_4O_6^=$ and $S_2O_3^=$. Heat of the reaction $I_3^- = I_2 + I^-$. Journal of the American Chemical Society 73: 1842-1843. 1951.

4. Bailey, N. et al. Structure and reactivity of the oxyanions of transition metals. Part VIII. Acidities and spectra of protonated oxyanions. Journal of the Chemical Society, 1960, p. 290-297.

5. Baxendale, J. H., E. M. Fielden and J. P. Kene. The pulse radiolysis of aqueous solutions of some inorganic compounds. Proceedings of the Royal Society, ser. A, 286:320-336. 1965.

6. Beard, Ralph F. and Nelson W. Taylor. The kinetics of the oxidation of iodide ion by acid dichromate solutions in presence of a neutral salt. Journal of the American Chemical Society 51:1973-1985. 1929.

7. Benson, Clara C. The rate of oxidation of ferrous salts by chromic acid. Journal of physical Chemistry 7:1-14. 1903.

8. Berthond, A. and Ch. Urech. Photoisomérisation de l'acide allocinnamique senssibilisee par l'iode. Helvetica Chimica Acta 13:437-444. 1930.

9. Bobtelsky, M. and A. Glasner. The oxidation of hydrobromic acid by chromic acid in the presence of manganese sulfate. Journal of the Chemical Society, 1948, p. 1376-1380.

10. Bobtelsky, von M. Über die Reaktionsgeschwindigkeit von Chromsäure und Jodwasserstoff in Gegenwart von neutralen Elektrolyten. Zeitschrift für Anorganische und Allgemeine Chemie 190:337-345. 1930.

11. Boyer, M. H. and J. B. Ramsey. Kinetics of the simultaneous reduction of oxygen and pervandyl ion by iodide ion in acid solution. Journal of the American Chemical Society 75:3802-3808. 1953.

12. Buxton, G. V. and F. S. Dainton. Radical and molecular yields in the γ-radiolysis of water. II. The potassium iodide-nitrous oxide system in the pH range 0 to 14. Proceedings of the Royal Society, ser. A, 287:427-443. 1965.

13. Chatterjee, K. and B. P. Gyani. Reduction of dichromates by iodide in presence of chlorides and bromides. Journal of the Indian Chemical Society 33:871-874. 1956.

14. Csanyi, László J. Simple method for estimating standard oxidation potentials and controlling their consistency on the basis of the Luther-Wilson rule. Magyar Kémiai Folyóirat 65:415-416. 1959. (Abstracted in Chemical Abstracts 54:14884c. 1960)

15. Daniele, Giorgio. Misura della constante de equilibrio del triioduro di potassio con un metodo spettrofotometrico. Gazzetta Chimica Italiana 90:1068-1081. 1960.

16. Davies, Mansel and Emrys Gwynne. The iodine-triiodide equilibrium in aqueous solutions. Journal of the American Chemical Society 74:2748-2752. 1952.

17. Davies, W. G. and J. E. Prue. A spectrophotometric study of the equilibrium $Cr_2O_7^{2-} + H_2O = 2HCrO_4^-$. Transactions of the Faraday Society 51:1045-1051. 1955.

18. DeLurry, Ralph E. The induction by arsenious acid of the reaction between chromic and hydriodic acids. Journal of Physical Chemistry 11:54-90. 1907.

19. _____ The rate of oxidation of potassium iodide by chromic acid. Journal of Physical Chemistry 7:239-253. 1903.

20. Diebler, H. and N. Sutin. The kinetics of some oxidation-reduction reactions involving manganese (III). Journal of Physical Chemistry 68:174-180. 1964.

128

21. Edwards, John O. Rate laws and mechanisms of oxyanion reactions with bases. Chemical Reviews 50:455-482. 1952.

22. Emerson, K. and W. M. Graven. Equilibria in acidic solutions of chromium (III) perchlorate. Journal of Inorganic and Nuclear Chemistry 11:309-313. 1959.

23. Espenson, James H. Kinetics and Mechanisms of the aquation of iodopentaaquochromium(III) ion and of oxidation of coordinated iodide ion in acidic solution. Inorganic Chemistry 3:968-972. 1963.

24. _____ Mechanisms of the reaction of vanadium(IV) and chromium(VI) and of the induced oxidation of iodide ion. Journal of the American Chemical Society 86:5101-5107. 1964.

25. Espenson, James H. and E. L. King. Kinetics and mechanisms of reactions of chromium(VI) and iron(II) species in acidic solution. Journal of the American Chemical Society 85:3328-3337. 1963.

26. Forbes, George S. and Arthur F. Nelson. Photoiodination of the butenes, propylene, and ethylene at low temperatures. Preparation and photolysis of 1, 2-Diiodiobutane. Journal of the American Chemical Society 59:693-697. 1937.

27. Fvennesson, S. Å., James Beattie and G. P. Haight, Jr. Mechanism of the reaction $HCrO_4^- + H_2PO_4^-$. (Abstract). American Chemical Society, Abstract of Papers 155:M13. 1968.

28. Graham, George T. E. and F. H. Westheimer. The kinetics of the chromic acid oxidation of benzaldehyde. Journal of the American Chemical Society 80:3030-3058. 1958.

29. Griffith, Robert Owen, Andrew McKeown and Albert Gordon Winn. The photo-reaction of oxalates with bromine and iodine. Part II. Theoretical. Transactions of the Faraday Society 29:386-395. 1933.

30. Haight, G. P., Jr., David C. Richardson and Nancy Hall Coburn. A spectrophotometric study of equilibria involving mononuclear chromium(VI) species in solutions of various acids. Inorganic Chemistry 3:1777-1780. 1964.

31. Haight, G. P., Jr. et al. The mechanism of the oxidation of sulfur(IV) by chromium(VI) in acid solution. Journal of the American Chemical Society 87:3835-3840. 1965.

32. Hampton, John, Albert Leo and F. H. Westheimer. The mechanism of the cleavage of phenyl-t-butylcarbinol by chromic acid. Journal of the American Chemical Society 78:306-312. 1956.

33. Haupt, G. W. An alkaline solution of potassium chromate as a transmittancy standard in the ultraviolet. Journal of Research of the National Bureau of Standards 48:414-423. 1952.

34. Hougen, Jon T., Kenneth Schug and Edward L. King. The isomeric dithiocyanatotetraaquochromium(III) ions; their separation, spectra and relative stabilities. Journal of the American Chemical Society 79:519-526. 1957.

35. Howard, J. R., V. S. K. Nair and G. H. Nancollas. Potentiometric and spectrophotometric studies of the equilibrium $HCrO_4^- = H^+ + CrO_4^{2-}$. Transactions of the Faraday Society 54:1034-1037. 1958.

36. Howlett, K. E. and S. Sarsfield. Kinetics and mechanism of redox reactions in aqueous solutions. Part II. The reaction between chromium(VI) and iodide. Journal of the Chemical Society, 1968, p. 683-686.

37. Jones, Grinnell and B. B. Kaplan. The iodide, iodine, triiodide equilbrium and the free energy of formation of silver iodide. Journal of the American Chemical Society 50:1845-1864. 1928.

38. Katzin, Leonard I. and Elizabeth Gebert. The iodide-iodine-triiodide equilibrium and ion activity coefficient ratios. Journal of the American Chemical Society 77:5814-5819. 1955.

39. Kemp, T. J. and William A. Waters. The catalysis by manganese ions of oxidations by aqueous chromic acid. Journal of the Chemical Society, 1964, p. 3193-3199.

40. Kice, John L. and Norman Pawlowski. The decomposition of aromatic sulfinyl sulfones (sulfinic anhydrides). The facile homolysis of a sulfur-sulfur bond. Journal of the American Chemical Society 86:4898-4903. 1964.

41. King, Edward L. and John A. Neptune. The interaction of chromium(III) and chromium(VI) in acidic solutions. Journal of the American Chemical Society 77:3186-3189. 1955.

42. Kolthoff, I. M. and Morton A. Fineman. Kinetics of the reaction between chromate and arsenic trioxide in alkaline medium. Induced reduction of oxygen by this couple. Journal of Physical Chemistry 60:1383-1388. 1956.

43. Kolthoff, I. M. and E. B. Sandell. Textbook of quantitative inorganic analysis. 3d ed. New York, Macmillan Company, 1952. 727p.

44. Lee, Donald G. and Ross Stewart. The nature of chromium(VI) in acid solution and its relation to alcohol oxidation. Journal of the American Chemical Society 78:3051-3056. 1964.

45. Linke, William F. (comp.). Solubilities, inorganic and metal-organic compounds; a compilation of solubility data from the periodical literature. 4th ed. Washington, D. C., American Chemical Society, 1965. 2 Vol.

46. Luther, R. and Th. F. Rutter. Zur Kenntnis der Oxydation-Reduktionsvorgänge. I. Reduktion der Chromsäure. Zeitschrift für Anorganische Chemie 54:1-30. 1907.

47. Mason, John G. and Albert D. Kowalak. The kinetics of the chromium(VI)-arsenic(III) reaction in acetic acid-acetate buffer solution. Inorganic Chemistry 3:1248-1251. 1964.

48. Mironov, V. E. and N. P. Lastovkina. Thermodyanics of triihalide ions. Russion Journal of Physical Chemistry 41:991-995. 1967.

49. Morgan, K. J. Some reactions of inorganic iodine compounds. The Chemical Society : Quarterly Reviews 81:123-146. 1954.

50. Neuss, Jacob D. and William Rieman. The application of the glass electrode to a study of chromic acid. Journal of the American Chemical Society 56:2238-2243. 1934.

51. Plane, Robert A. and John P. Hunt. Photochemical exchange of water between $Cr(H_2O)_6^{3+}$ and solvent. Journal of the American Chemical Society 79:3343-3346. 1957.

52. Preer, James and G. P. Haight, Jr. On the inertia of aqueous phosphite ion to oxidation. Journal of the American Chemical Society 87:5256-5257. 1965.

53. Pungor E. and J. Trompler. Die Rolle der Säurenkonzentration bei Oxydationen mittel Chromats. Journal of Inorganic and Nuclear Chemistry 5:123-132. 1957.

54. Roček, Jan and Annette E. Radkowsky. The role of chromium(IV) in oxidation of chromic acid. The oxidative cleavage of cyclobutanol. Journal of the American Chemical Society 90:2986-2988. 1968.

55. Seubert, K. and J. Karstens. Zur Kenntnis der Chromsäure als Oxydationsmittel. Zeitschrift für Anorganische Chemie 50:53-66. 1906.

56. Shevchenko, V. B., I. V. Shilin and Yu F. Zhdanov. Behavior of hexavalent and trivalent chromium during the extraction of uranyl and plutonium nitrates with tributyl phosphate. Russian Journal of Inorganic Chemistry 5:1367-1371. 1960.

57. Stewart, Ross. Oxidation mechanisms: applications to organic chemistry. New York, W. A. Benjamin, 1964. 179 p.

58. Swaddle, Thomas W. and E. L. King. The rate of aquation of halopentaaquochromium(III) ion in acidic aqueous solution. Inorganic Chemistry 4:532-538. 1965.

59. Tong, James Yingpeh. Chromium(VI) species and spectra in acidic solution. Inorganic Chemistry 3:1804-1805. 1964.

60. Tong, James Yingpeh and Ray L. Johnson. The dissociation equilibria of trioxochlorochromate(VI) and chromic acid. Inorganic Chemistry 5:1902-1906. 1966.

61. Tong, James Yingpeh and Edward L. King. The kinetics and mechanism of the reaction of cerium(IV) and chromium(III). Journal of the American Chemical Society 82:3805-3809. 1960.

62. _____ A spectrophotometric investigation of the equilibria existing in acidic solution of chromium(VI). Journal of the American Chemical Society 75:6180-6186. 1953.

63. Tsachihashi, G. et al. The kinetics of the reactions of acyl peroxides with alkali iodides--I. The reactions of aroyl peroxides with potassium iodide. Tetrahedron 21:1039-1048. 1965.

64. Waters, W. A. Evidence for the dehydration theory of oxidation. Transactions of the Faraday Society 42:184-190. 1946.

65. _____ A study of the mechanisms of oxidation with chromic acid. Journal of the Chemical Society, 1946, p. 1151-1154.

66. Watanabe, Warren and F. H. Westheimer. The kinetics of the chromic acid oxidation of isopropyl alcohol : The induced oxidation of manganeous ion. Journal of Chemical Physics 17:61-70. 1949.

67. Westheimer, F. H. Mechanism of chromic acid oxidations. Chemical Review 45:419-451. 1949.

68. Wiberg, Kenneth B. (ed.). Oxidations in organic chemistry. Part A. New York, Academic Press, 1965. 443 p.

69. Wiberg, Kenneth B. and Theodore Mill. The kinetics of the chromic acid oxidation of benzaldehyde. Journal of the American Chemical Society 80:3022-3029. 1958.

70. Wiberg, K. B. and W. H. Richardson. The chromic acid oxidation of aromatic aldehydes. Some observations concerning the oxidation by the chromium species of intermediate valence. Journal of the American Chemical Society 84:2800-2807. 1962.

71. Wu, Ching-Hsien, Merritt M. Birky and Loren G. Hepler. Thermochemistry of some bromine and iodine species in aqueous solution. Journal of Physical Chemistry 67:1202-1205. 1963.

APPENDIX

APPENDIX

Least Squares Analysis for One to Six Independent Variables

The first order rate constant, k_{obs}, can be set equal to a series

of independent values, $(k_1, k_2, k_3, \cdots)$ in which the hydrogen and

iodide ion concentrations are the variables.

$$k_{obs} = k_1 [H^+]^t [I^-]^v + k_2 [H^+]^w [I^-]^x + k_3 [H^+]^y [I^-]^z + \cdots$$

The computer program was written so that one to six of these terms

could be used. The number of independent constants is represented

by IV.

For a least squares analysis the quantity $\Sigma (k_{obs} - k_{calc})^2$ is

made a minimum

$$2\Sigma (k_{obs} - k_{calc}) \times dk_{calc} = 0$$

in which k_{calc} is the calculated first order rate constant from the

trial rate law. If IV is taken to be three, the most common number

in the trials, and if A_i represents $[H^+]^n [I^-]^m$, the equations are:

$$k_{calc} = k_1 A_1 + k_2 A_2 + k_3 A_3$$

$$\frac{dk_{calc}}{dk_i} = \frac{\partial k_{calc}}{\partial k_1} + \frac{\partial k_{calc}}{\partial k_2} + \frac{\partial k_{calc}}{\partial k_3}$$

A weighting factor must be placed in this analysis so that the slow

runs, smaller k_{obs} values, are given equal weight compared to the

fast runs. The weighting factor is defined as $WF = X/k_{obs}$ in which

$X = 1.0 \times 10^{-3}$. Both sides of the equation are multiplied by WF.

$$k_{calc} \cdot (WF) = k_1 A_1 (WF) + k_2 A_2 (WF) + k_3 A_3 (WF)$$

From these equations, three equations with three unknowns are obtained since:

$$\Sigma (k_{obs} - k_{calc}) \frac{\partial k_{calc}}{\partial k_i} = 0, \text{ when } \frac{\partial k_{calc}}{\partial k_i} = A_i (WF)$$

The resulting equations are:

$$\Sigma (k_1 A_1^2 (WF)^2 + k_2 A_1 A_2 (WF)^2 + k_3 A_1 A_3 (WF)^2) = \Sigma k_{obs} A_1 (WF)^2$$

$$\Sigma (k_1 A_1 A_2 (WF)^2 + k_2 A_2^2 (WF)^2 + k_3 A_2 A_3 (WF)^2) = \Sigma k_{obs} A_2 (WF)^2$$

$$\Sigma (k_1 A_1 A_3 (WF)^2 + k_2 A_2 A_3 (WF)^2 + k_3 (A_3)^2 (WF)^2) = \Sigma k_{obs} A_3 (WF)^2$$

A matrix is set up with $B_{ij} = \Sigma A_i A_j (WF)^2$ and $C_i = \Sigma k_{obs} A_i (WF)^2$:

$$k_1 B_{11} + k_2 B_{12} + k_3 B_{13} = C_1$$

$$k_1 B_{21} + k_2 B_{22} + k_3 B_{23} = C_2$$

$$k_1 B_{31} + k_2 B_{32} + k_3 B_{33} = C_3$$

Using a Matrix inversion, the solutions for the k_1, k_2, and k_3 are determined by:

$$B \times \begin{Bmatrix} k_1 \\ k_2 \\ k_3 \end{Bmatrix} = C$$

The matrix inversion is accomplished by a subroutine in the

computer. Different values of X resulted in the same k_i values; therefore, the values of k_i are independent of X.

The dispersion error of the correlation is defined as:

$$S = [\Sigma(k_{obs} - k_{cal})^2 (WF)^2 / (n - IV)]^{1/2}$$

in which n = total number of independent kinetic runs. The S depends upon the value of X chosen to define WF, but the ratio s/X does not depend on this value of X. The standard error for each rate constant is determined by:

$$\text{Standard error in } k_i = S \cdot \sqrt{B_{jj}^{-1}}$$

These values do not depend on WF. The definitions of dispersion and standard error are given by Arley and Buck (2).