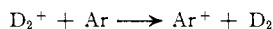lationship is satisfied

$$\frac{|\Delta E|a}{hv_{rel}} \approx 1$$

where $|\Delta E|$ is the energy defect, a is a parameter and is usually taken as about 7 Å., and v_{rel} is the relative velocity of the ion. As pointed out by Sluyters, et al.,[18] this picture depends strongly on the value for $|\Delta E|$. Wolf[4] examined the reaction

$$D_2^+ + Ar \longrightarrow Ar^+ + D_2$$

and found a maximum at 1.18 e.v. He assumed the D_2^+ was in the $v = 0$ state and used an energy defect of 0.3 e.v.

It can be seen from Fig. 3 that there are several maxima on the cross-section curve. This may be explained in the light of recent interpretations of the role of higher vibrational states of H_2^+ in ion–molecule reactions.[19-23] von Koch and Friedman[19] calculated the population of the vibrational states of H_2^+ when it is formed by H_2 by the bombardment of 50-e.v. electrons. They found the upper states (to $v = 4$) to have a significant population. Kraus and Kopf[22]

(18) Th. J. M. Sluyters, E. de Haas, and J. Kistemaker, Physica, 25, 1376 (1959).
(19) H. von Koch and L. Friedman, J. Chem. Phys., 38, 1115 (1963).
(20) S. Kerwin, P. Marmet, and E. Clarke, Can. J. Phys., 39, 1240 (1961).
(21) P. Marmet and L. Kerwin, ibid., 38, 972 (1960).
(22) M. Kraus and A. Kopf, J. Chem. Phys., 26, 1776 (1957).
(23) A. Weingartshofer and E. Clarke, Phys. Rev. Letters, 13, 591 (1964).

calculated the transition probabilities from the molecular ground state to various vibrational levels in the molecule ion and found them to be: 0.44, 0.87, 1.00, 0.91, and 0.72. Kerwin, et al.,[20] measured these transition probabilities and generally corroborated the results. Various investigators have also used vibrationally excited states in charge-transfer reactions.[18,24]

The lifetime of some vibrational states of HD^+ have been measured at around 200 μsec.[25] Thus, it is almost certain that the HD^+ is formed in vibrationally excited states and that these states live long enough to allow the molecule ion to react in excited states. This makes several values available for $|\Delta E|$ in the charge-transfer process. Thus, although there may be some ambiguity in assigning the observed peaks to particular vibrational states, the observed structure in the cross-section curve suggests that HD^+ ions in the $v = 0, 1, 2, 3$, and perhaps $v = 4$ states are reacting with argon in the charge-exchange process.

In conclusion, therefore, this study reveals an isotope effect in the reaction $HD^+ + Ar \rightarrow$ argon hydrides which is compatible with deductions obtained by considering the conservation of energy and angular momentum in this reaction. In the charge-exchange reaction, the measurements support the idea that vibrationally excited states are involved in the process.

(24) E. Gustafson and E. Lindholm, Arkiv Fysik, 18, 219 (1960).
(25) J. R. Hiskes, Phys. Rev., 122, 1207 (1961).

Mechanisms of the Reaction of Vanadium(IV) and Chromium(VI) and of the Induced Oxidation of Iodide Ion[1]

BY JAMES H. ESPENSON

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The 3-equiv. reaction between vanadium(IV) and chromium(VI) in acidic perchlorate solution follows the rate equation

$$-d[HCrO_4^-]/dt = [VO^{2+}]^2[VO_2^+]^{-1}\{k[HCrO_4^-] + k'[H^+][HCrO_4^-]^2\}$$

at 25° and ionic strength 1.00 F, $k = 0.563$ M^{-1} sec.$^{-1}$ and $k' = 5.4 \times 10^4$ M^{-3} sec.$^{-1}$. A mechanism consistent with the first term involves a sequence of three 1-equiv. reactions, in which chromium(V) is an unstable intermediate. The k' pathway presumably involves reaction of dichromate ion along a similar reaction sequence. These postulated mechanisms are compared with results on related systems. The oxidation of iodide ion induced by this reaction is interpreted in terms of its competition for the intermediate chromium(V), and ratios of rate constants are obtained by the study of apparent stoichiometry of the induced reaction. Combination of these results and data from earlier studies on related systems allows some conclusions to be drawn concerning the role of hydrogen ion in several reaction steps.

Introduction

The over-all oxidation–reduction reaction in which chromium(VI) oxidizes vanadium(IV) to vanadium(V) is not expected to occur in a single step, since chromium undergoes a change of three units in oxidation number.

$$3VO^{2+} + HCrO_4^- + H^+ = 3VO_2^+ + Cr^{3+} + H_2O \quad (1)$$
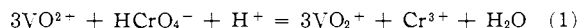
For this reason, the mechanism involves a sequence of less complex elementary reaction steps. Intermediate oxidation states of chromium are expected to play an important role in the mechanism. A preliminary

communication of portions of this work has already appeared.[2]

With regard to stoichiometry, this reaction is similar to two previously studied reactions, iron(II)–chromium(VI)[3] and cerium(IV)–chromium(III).[4] Both these latter reactions follow essentially the same pattern: reduction of chromium(V) to chromium(IV), or the reverse, is the slowest step in a reaction sequence made up of three 1-equiv. changes.

A thorough study of the kinetic behavior of the vanadium(IV)–chromium(VI) reaction was under-

(2) J. H. Espenson, J. Am. Chem. Soc., 86, 1883 (1964).
(3) J. H. Espenson and E. L. King, ibid., 85, 3328 (1963).
(4) J. Y.-P. Tong and E. L. King, ibid., 82, 3805 (1960).

taken in the interest of finding whether or not the same sort of reaction sequence is also observed here. Studies of the induced oxidation of iodide ion will also shed light on the intermediates involved.[5] The vanadium(IV)–vanadium(V) and the iron(II)–iron(III) couples are related by a known difference in Gibbs free energy, and it is possible to combine two sets of kinetic results to obtain an independent value for this ΔG, thus providing a very useful cross check on these two systems.

Experimental

Reagents.—A vanadium(IV) perchlorate stock solution (0.1 F) was prepared from equivalent amounts of vanadyl sulfate (Fisher Scientific Co.) and barium perchlorate in concentrated solution. Precipitated barium sulfate was removed by filtration through a fine sintered-glass funnel. Alternatively, a vanadium(IV) solution (0.07 F) was prepared from vanadium pentoxide in 0.2 F perchloric acid by electrolytic reduction at a mercury cathode. Reduction was carried a little beyond the +4 state to obtain complete dissolution of vanadium pentoxide. To remove the vanadium(III) formed in this preparation, a dilute solution of vanadium(V) was added until tests on the resulting solution showed neither vanadium(III) nor vanadium(V). These tests consisted of adding the acidic vanadium solution to aqueous iodide ion or iodate ion. Lack of iodine color in a carbon tetrachloride layer indicates absence of vanadium(V) and -(III), respectively. Vanadium(V) solutions (0.01 F) were prepared by dissolving the pentoxide in perchloric acid. The vanadium pentoxide used in the vanadium(IV) preparation and in some of the vanadium(V) solutions was a special preparation made by hydrolysis with aqueous ammonia of fractionally distilled VOCl₃; the ammonium vanadate was ignited to the oxide.[6] Potassium dichromate, A.R. grade, was dried at 150° and used directly, and another sample was first recrystallized from water three times before drying. Lithium perchlorate (G. F. Smith) was recrystallized twice from water. Reagent grade perchloric acid (Baker, 72%) and sodium iodide were used without further purification. Conductivity water, a redistillation of laboratory-distilled water from alkaline permanganate in a tin-lined still (Barnstead Co.), was used throughout.

Analysis for vanadium(V) was by direct titration in sulfuric acid solution with iron(II) using diphenylamine as indicator. Analysis for vanadium(IV) was made by prior oxidation with permanganate. Excess permanganate was destroyed by nitrous acid, then the excess nitrous acid by sulfamic acid.[7] The solution was titrated with iron(II) as before. Direct titration of vanadium(IV) with permanganate at 70° was also used, but the permanganate end point at this elevated temperature generally proved less satisfactory than the indirect procedure outlined above.

Kinetic Experiments.—All reagents except chromium(VI) were added to a 10-cm. spectrophotometer cell which was then sealed with a rubber serum cap. The solution and cell were brought to reaction temperature (25.00° throughout) by immersion to the capped filling neck in a thermostated water bath. The cell was then transferred to a specially designed, water-filled cell jacket positioned in the compartment of a Cary Model 14 recording spectrophotometer. In this jacket the cell is actually immersed in water up to the filling neck. Water from the constant temperature bath circulates through insulated tubing and around the outer compartment of the metal cell jacket.[8] The intimate contact between thermostating medium and reaction vessel assures temperature uniformity and precise control. Experiments using a calorimetric thermometer graduated in 0.01°

intervals indicated that the temperature of the water in which the silica reaction cell sits is constant to within 0.01° over periods in excess of 1 hr.

The required volume of chromium(VI) solution, also at 25.00°, was taken in a calibrated 1-ml. hypodermic syringe and added through the rubber cap. The solution was mixed and a recording made of absorbance vs. time at a particular fixed wave length.

Extent of Reaction.—Concentrations as a function of time were measured spectrophotometrically. Molar extinction coefficients, a, were evaluated at room temperature, in solutions 0.005–0.1 F HClO₄, with ionic strength maintained at 1.0 F by lithium perchlorate. Concentrations of chromium(VI) at various times during a run were calculated from the relation

$$[Cr^{VI}] = (A - A_\infty)/b\Delta a \qquad (2)$$

A represents a measured absorbance value during the run, A_∞ is this quantity at equilibrium, and b is the optical path length (10 cm. throughout). The equation

$$\Delta a = a_{HCrO_4^-} + 3a_{VO^{2+}} - a_{Cr^{3+}} - 3a_{VO_2^+} \qquad (3)$$

defines Δa.

Table I presents values of the molar extinction coefficients measured here for each species at the several wave lengths of interest. This table also presents the calculated values of Δa.

Table I

MOLAR EXTINCTION COEFFICIENTS (M^{-1} CM.$^{-1}$) AT DIFFERENT WAVE LENGTHS IN 0.01–0.05 F PERCHLORIC ACID

Species	3130 Å.	3500 Å.	4320 Å.	7640 Å.
HCrO₄⁻ᵃ	711.2	1558 (max.)	226 (max.)	0
VO²⁺	10.7	0	0	17.04 (max.)
Cr³⁺	0.5	3.2	11.9	0
VO₂⁺	400.2	140.6	5.8	0
Δa^b	−457	1133	197	51.12

ᵃ Chromium(VI) concentrations in runs studied at the wave lengths 7640 and 4320 Å. were sufficiently large that appreciable dichromate ion was present; this had little, if any, effect on the absorbance. The chromium(VI) concentrations in runs at the lower wave lengths were sufficiently low that hydrogen chromate ion was the only species present at significant concentration. ᵇ Defined by eq. 3.

Instantaneous concentrations of other reactants and products were computed from the initial concentrations and the calculated chromium(VI) concentration, assuming the reaction occurs according to the stoichiometry in reaction 1 and that no interactions between various species occur. Calculated and observed equilibrium absorbances generally differ by less than 0.01 absorbance unit (for a 10-cm. path) and never exceeded 0.03. In each run the experimental value of A_∞ was used in eq. 2 to calculate chromium(VI) concentrations.

Experiments between several pairs of the species involved were performed to establish whether appreciable complex formation occurs. These experiments consisted of spectrophotometric examination of such combined solutions and of the separate components. The pairs examined in this fashion were: vanadium(V)–chromium(III), vanadium(V)–chromium(VI), and vanadium(IV)–chromium(III). In each instance the absorbance values measured for the combined solutions were in agreement with the value calculated assuming no interaction. Previous work has established that chromium(III) and chromium(VI) interact in acidic solution.[9] These results indicate that the enhanced absorbances in chromium(III)–(VI) mixtures are due to CrCrO₄⁺, which exhibits strong light absorption despite its presence at only insignificant concentration. Under conditions of the present experiments it contributes negligibly to the absorbance. The rapid reaction of vanadium(IV) and chromium(VI) has prevented a direct study of possible interaction of this pair. At wave length 7640 Å. the absorbance is due primarily to vanadium(IV), and at 4320 Å. primarily to chromium(VI) (Table I). Reaction rates of pairs of identical solutions were measured at both wave lengths. The results at both wave lengths were interpreted on the basis that (a) an inappreciable concentration of any complex forms, and (b) there is no intensely absorbing complex species present at very low concentration (as in the chromium-

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

(6) The author is grateful to Dr. R. E. McCarley of Iowa State University for this specially purified sample of vanadium pentoxide.

(7) H. R. Grady in "Treatise on Analytical Chemistry," Vol. VIII, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Part II, p. 227.

(8) The author wishes to acknowledge the advice of Dr. Thomas W. Newton on this thermostating arrangement. A commercial cell jacket, Applied Physics Corp. No. 1444100, was modified by affixing a quartz plate over each end window space and rendering the entire apparatus water tight. The absorbance contribution of the several millimeters of water thus in the light path when a 10-cm. cell is used is generally quite small and is compensated precisely by the zero adjustment.

(9) E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

(III)–(VI) case cited above). Agreement of the kinetic parameters for several pairs of such solutions has been taken as evidence for the validity of these assumptions.

Analyses for iodine(0) were performed spectrophotometrically at 4650 Å. This wave length is a maximum for I_2, and I_3^- also absorbs appreciably. In most experiments the concentration of free iodide ion was such that both I_2 and I_3^- were present at comparable concentration, both usually much lower than $[I^-]$. This analytical method for total iodine was calibrated as a function of $[I^-]$ using known solutions: these data lead to values for the apparent extinction coefficient of iodine(0) as a function of iodide ion concentration. Vanadium(IV) and -(V) and chromium(III) do not interfere with the spectrophotometric analysis, provided it is made within *ca.* 15 min. of mixing, so that inappreciable reaction of vanadium(V) and iodide ion occurs.

Results

Reaction Stoichiometry.—Agreement between observed and calculated values of absorbance at equilibrium has been noted. The calculated value assumes the stoichiometry represented by reaction 1, at least with regard to oxidation–reduction equivalents. This is apparently justified. Hexaaquochromium(III) ion, rather than a polymerized chromium(III) species,[10] is a reaction product. This anticipated result was established by cation-exchange experiments on reaction solutions which had come to equilibrium. After vanadium(IV) and -(V) were eluted from the resin column with 1.5 *F* perchloric acid, the chromium(III) band was eluted slowly with 3 *F* perchloric acid. Visual observations indicated that the hexaaquo ion is the only significant chromium(III) product.

Concentration Conditions and Predominant Species in Kinetic Experiments.—The kinetics of this reaction were studied over as wide a range of reactant and product concentrations as practicable by these experimental techniques. Variations in "initial" (first measured point) concentrations were as follows. Vanadium(V) varied from 3×10^{-5} to 1.4×10^{-2} (500-fold), vanadium(IV) from 4×10^{-4} to 1×10^{-2} (25-fold), and chromium(VI) from 5×10^{-5} to 1.5×10^{-3} *F* (30-fold). If concentration changes during measured portions of kinetic runs are also considered, each of these variations is increased by about another factor of 2 (vanadium species) to 5 (chromium(VI)). Perchloric acid concentrations were in the range 0.005–0.10 *F*. Ionic strength was maintained at 1.0 *F* in all experiments with lithium perchlorate.

Rossotti and Rossotti have presented extensive studies of the acid–base equilibria in acidic solutions of vanadium(IV)[11] and vanadium(V).[12] They conclude that the species VO^{2+} dominates in vanadium(IV) perchlorate solutions at these acid concentrations. Likewise, in these acidic solutions monomeric VO_2^+ (or $V(OH)_4^+$) is the dominant vanadium(V) species. At the highest vanadium(V) concentration and lowest hydrogen ion concentrations studied here appreciable acid dissociation and polymerization of vanadium(V) occur.[12] These extremes were not studied simultaneously in kinetic experiments to avoid ambiguity arising from the presence of such species.
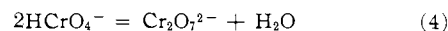
Under the conditions of these experiments two chromium(VI) species are important, $HCrO_4^-$ and $Cr_2O_7^{2-}$.

The rapidly established dimerization equilibrium

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O \qquad (4)$$

has been studied spectrophotometrically.[13] Under the conditions of the present work (25.0° and unit ionic strength), the concentration equilibrium quotient is $Q_D = 98$ M^{-1}. This equilibrium, the position of which depends only upon the formal concentration of chromium(VI), must be taken into account in formulating the rate law in terms of concentrations of species.

Interpretation of Kinetic Data.—Either of two equivalent equations

$$-d[Cr^{VI}]/dt = ([VO^{2+}]^2/[VO_2^+])\{k[HCrO_4^-] + k'[H^+][HCrO_4^-]^2\} \quad (5)$$

$$= ([VO^{2+}]^2/[VO_2^+])\{k[HCrO_4^-] + k'Q_D^{-1}[H^+][Cr_2O_7^{2-}]\} \quad (6)$$

describes the kinetic behavior of reaction 1 under all conditions of concentration studied. Different methods were used here to treat the kinetic data to establish this rate equation and to evaluate k and k', depending upon the relative contribution of the two terms.

At low concentrations of chromium(VI), $<2 \times 10^{-4}$ *F*, the species hydrogen chromate ion accounts for $\geq 98\%$ of this concentration (it is *not* necessarily true, however, that at the same time the term first order in $[HCrO_4^-]$ constitutes the major reaction pathway). In all experiments where the first rate law term dominates throughout the run (at chromium-(VI) concentrations $\leq 4 \times 10^{-5}$ *F* below 0.03 *M* H^+) k is evaluated as the slope of a plot of the integrated rate equation[14] *vs.* time. The mean value of k (evaluated in each experiment by the method of averages) from 17 experiments with $[H^+]$ in the range 0.005–0.030 *M* is 0.563 M^{-1} sec.$^{-1}$ (± 0.039 standard deviation). Individual rate constants for the experiments in this series show no apparent trends with vanadium(IV), vanadium(V), or hydrogen ion concentration.[15] At higher $HClO_4$ concentrations this treatment is not valid, and the graphs for the integrated rate equation are not linear, since the k' term exerts substantial influence even at lower chromium-(VI) concentration.

When the product $[HCrO_4^-][H^+]$ exceeds *ca.* 2×10^{-6}, noticeable deviations from the one-term rate equation occur. Such deviations exhibit themselves in two ways. Let k_{app} represent an apparent rate constant, defined by the equation

$$k_{app} = [VO_2^+][VO^{2+}]^{-2}[Cr^{VI}]^{-1}d[Cr^{VI}]/dt \quad (7)$$

The deviations observed at these higher chromium(VI) concentrations are: (a) k_{app} gradually decreases with increasing extent of reaction (*i.e.*, the apparent reaction order with respect to chromium(VI) is a function of its concentration), and (b) k_{app} is consistently and substantially larger than the value of k for all the experiments at low chromium(VI). These observations are related. As chromium(VI) decreases in concentration during a run, the fraction existing as dichromate ion decreases, accounting for the decrease in k_{app}.

(10) M. Ardon and R. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

(11) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

(12) F. J. C. Rossotti and H. Rossotti, *ibid.*, **10**, 957 (1956).

(13) J. Y.-P. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

(14) This complicated equation is analogous to eq. 9 of ref. 3 and eq. 4 of ref. 4.

(15) The mean value of k reported here is *ca.* 10% less than that reported in the preliminary communication (ref. 2).
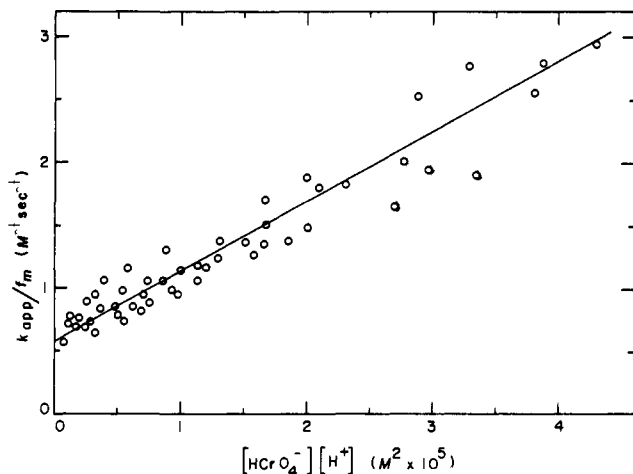
Fig. 1.—Linear plot of k_{app}/f_m vs. $[HCrO_4^-][H^+]$ illustrating conformity of data to eq. 5 and 8.

This is also consistent with the second observation that k_{app} is always larger than the previously established value of k, 0.56 M^{-1} sec.$^{-1}$, provided there is a parallel reaction pathway involving dichromate ion.

Treatment of these data to establish that eq. 5 and 6 do, in fact, describe the kinetic behavior over the entire range of conditions was carried out as follows. Combination of eq. 5 and 7 leads to the result in which

$$k_{app}/f_m = k + k'[HCrO_4^-][H^+] \qquad (8)$$

f_m represents the fraction of the formal chromium(VI) concentration existing as monomeric $HCrO_4^-$, $f_m = [HCrO_4^-]/[Cr^{VI}]$. Values of k_{app} were obtained as instantaneous slopes of $[VO_2^+][VO^{2+}]^{-2}[Cr^{VI}]^{-1}d$-$[Cr^{VI}]$ vs. time; evaluation of this integral was made as before.[14] Both f_m and $[HCrO_4^-]$ were calculated from the instantaneous formal chromium(VI) concentration, at the point where the slope was measured, using $Q_D = 98$ M^{-1} for reaction 4. In this fashion a series of points (k_{app}/f_m), $[HCrO_4^-]$ is obtained for each run at the higher chromium(VI) concentrations. The collection of points from all appropriate runs was plotted according to eq. 8 and a selection of these points are shown in Fig. 1. The slope, k', is $5.4 \pm 0.6 \times 10^4$ M^{-3} sec.$^{-1}$. The intercept of this plot is identified in eq. 8 as k. The value obtained $(0.57 \pm 0.05$ M^{-1} sec.$^{-1})$ from these runs agrees with the value $(0.563$ M^{-1} sec.$^{-1})$ from the runs in which only this term contributes appreciably. The considerable scatter in this plot reflects, in part, the difficulties associated with measuring instantaneous slopes in rate plots. Since the scatter appears random, and not a function of vanadium concentrations, the concentration dependences of the k' term given in eq. 5 are assumed to be correct.

Induced Oxidation of Iodide Ion.[16]—As was noted in earlier work,[17] iodide ion is oxidized quite rapidly during the occurrence of the main reaction between chromium(VI) and vanadium(IV). Although iodide ion is slowly oxidized to triiodide ion by both chromium(VI)[18] and vanadium(V)[19] in acidic solution, the

(16) The subject of reactions induced by chromium(VI) oxidation reactions has been reviewed by Westheimer, ref. 5.
(17) R. Luther and T. F. Rutter, Z. anorg. Chem., **54**, 1 (1907).
(18) R. F. Beard and N. W. Taylor, J. Am. Chem. Soc., **51**, 1973 (1929).
(19) J. B. Ramsey, E. L. Colichman, and I. C. Pack, ibid., **68**, 1695 (1946).

rates of these reactions are very much lower than observed for the oxidation of iodide here. The latter process is essentially instantaneous at the concentrations employed here. The evidence that this is not merely a case of vanadium(IV) acting as a catalyst for the reaction of chromium(VI) and iodide ion is: (a) vanadium(IV) is, itself, oxidized during the over-all reaction, (b) the amount of iodide oxidized relative to vanadium(IV) oxidized *decreases*, and not increases, when the vanadium(IV) concentration is increased, and (c) the relative amounts of iodide and vanadium(IV) oxidized approach a definite limit as the concentration ratio, $[I^-]/[VO^{2+}]$, increases. A quantity called the induction factor, F_i, defined as the ratio of iodide ion oxidized to vanadium(IV) oxidized, provides a convenient description of the system. Solutions having known $[I^-]/[VO^{2+}]$ ratios were reacted with a low concentration (ca. 10^{-4} F) of chromium(VI) and the stoichiometry established by analysis. (The iodine(0) content was analyzed spectrophotometrically; the amount of vanadium(IV) oxidized is the difference between the total equivalents of chromium-(VI) added and those of iodine formed.) Values of the ratio F_i were thus obtained in different experiments as a function of the $[I^-]/[VO^{2+}]$ ratio. Table II presents results of the series at 0.0050 F perchloric acid. These data illustrate the asymptotic approach of F_i to 2.00 with increasing $[I^-]/[VO^{2+}]$.

TABLE II

INDUCED OXIDATION OF IODIDE ION[a,b]

$[VO^{2+}]_0(M \times 10^4)$	$[I^-]/[VO^{2+}]^c$	$F_i{}^d$
48.9	0.19	0.81, 0.87
48.9	0.21	1.01
19.5	0.37	1.13, 1.15, 1.23
9.8	0.47	1.29
19.5	0.52	1.29
19.5	1.04	1.39
9.8	1.04	1.61
9.8	2.10	1.73
9.8	4.22	1.90
4.9	4.26	1.87
9.8	8.38	1.97

^{a} 0.0050 F perchloric acid. ^{b} 25.0°, ionic strength 1.0 F (LiClO$_4$ + HClO$_4$). ^{c} This ratio is generally fairly constant ($\pm 10\%$) during a run; the tabulated ratio is the initial value. ^{d} Iodide ion oxidized/vanadium(IV) oxidized.

Similar data at other perchloric acid concentrations in the range 0.0025–0.030 F establish that F_i depends upon $[H^+]$ in addition to its dependence upon $[I^-]/[VO^{2+}]$. At higher $[H^+]$, F_i approaches its limit of 2.00 at even lower values of the ratio $[I^-]/[VO^{2+}]$. The quantitative dependence of F_i is such that a plot of $F_i^{-1} - ([Cr^{VI}]_0/2C_{I_2})$ vs. $[VO^{2+}][H^+]^{-1}[I^-]^{-1}$ is linear. Figure 2 shows all the data for F_i plotted in this fashion. The significance of the linearity of such a plot will be shown later.
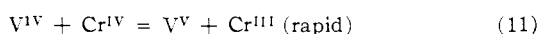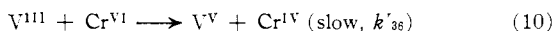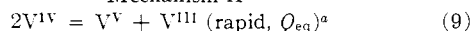
Interpretation and Conclusions

The Rate Law Term First Order in Chromium(VI).— The first term in eq. 6 carries the bulk of reaction at low concentrations of hydrogen chromate and hydrogen ions. Mechanisms consistent with the term $k[VO^{2+}]^2$-$[HCrO_4^-][VO_2^+]^{-1}$ involve transition states with composition $(HCrO_4V^{2+} \pm nH_2O)^*$. A suitable mechanism requires that one VO_2^+ be produced in an equilibrium step before the rate-determining step; this
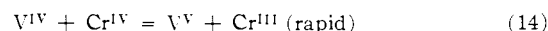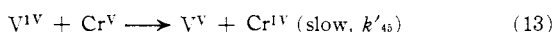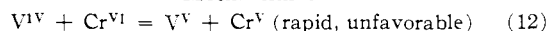
feature is required by the experimentally observed negative first-order dependence upon vanadium(V). The form of the rate law also establishes the average oxidation number of chromium and vanadium in the transition state of the rate-limiting step; this average is $4.5[0.5(2 \times 4 + 6 - 5)]$. Two likely combinations lead to this average, $Cr^{VI}-V^{III}$ and $Cr^{V}-V^{IV}$. These considerations suggest two mechanisms which fulfill all kinetic requirements. Written in terms of oxidation numbers, rather than species, these mechanisms are as shown in Scheme I.

Scheme I
Mechanism A

$$2V^{IV} = V^{V} + V^{III} \text{ (rapid, } Q_{eq})^{a} \tag{9}$$

$$V^{III} + Cr^{VI} \longrightarrow V^{V} + Cr^{IV} \text{ (slow, } k'_{36}) \tag{10}$$

$$V^{IV} + Cr^{IV} = V^{V} + Cr^{III} \text{ (rapid)} \tag{11}$$

Mechanism B

$$V^{IV} + Cr^{VI} = V^{V} + Cr^{V} \text{ (rapid, unfavorable)} \tag{12}$$

$$V^{IV} + Cr^{V} \longrightarrow V^{V} + Cr^{IV} \text{ (slow, } k'_{45}) \tag{13}$$

$$V^{IV} + Cr^{IV} = V^{V} + Cr^{III} \text{ (rapid)} \tag{14}$$

$^{a} Q_{eq} = k'_{44}/k'_{35} \ll 1.$

Proposal A involves disproportionation of vanadium(IV), known to be quite unfavorable, followed by 2-equiv. oxidation of vanadium(III). (Such 2-equiv. steps have been substantiated in some chromium(VI) oxidations.[5]) Proposal B involves a sequence of three 1-equiv. reactions. The observed rate law does not provide a basis on which these two mechanisms can be distinguished, *nor should it be expected to do so,* for both satisfy all basic information provided by the kinetic study, namely, both lead to the same composition for the transition state in the rate-determining step.

An additional point of experimental evidence aids in eliminating one of these proposed reaction paths. This has to do with the identification of the apparent rate constant k, on the basis of mechanism A. In that instance k is identified as $Q_{eq}k'_{36}$. Since standard oxidation potential values allow calculation of Q_{eq} for the disproportionation of vanadium(IV), k'_{36} can be estimated. At 25°, Q_{eq} has the value 10^{-10}; thus k'_{36} would be $0.56 \times 10^{10} M^{-1}$ sec.$^{-1}$. Now the observed rate law imposes upon the rate constants associated with mechanism A the requirement that the reverse of the first step be relatively much more rapid than the forward of the second; that is, that the fate of the unstable vanadium(III) intermediate generally be to react with vanadium(V) and not with chromium(VI). Expressed in terms of appropriate rate constants and concentrations, if mechanism A is to be consistent with experiment, then $k'_{35}[V^{V}] \gg k'_{36}[Cr^{VI}]$. The reaction of vanadium(III) and vanadium(V) has been studied by Daugherty and Newton[20]; the value of k'_{35}, the apparent second-order rate constant at 25° and $0.02 M H^{+}$, is $k'_{35} \cong 1.4 \times 10^{4} M^{-1}$ sec.$^{-1}$ (by extrapolation). For the required inequality to hold, it would be necessary that $[V^{V}]/[Cr^{VI}] \gg 4 \times 10^{5}$, a condition generally far from satisfied in these experiments. On this basis, then, mechanism A is discarded from further consideration.

The explanation has been offered[4] in reactions similar to this, that chromium(V) and -(IV) differ in coordina-
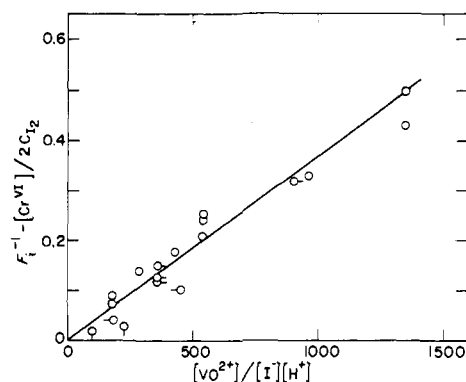
(20) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **68**, 612 (1964).

Fig. 2.—Data on the induced oxidation of iodide ion, plotted according to eq. 24; ○, $0.0050 M H^{+}$; ⊖, $0.0075 M H^{+}$; ⊝, $0.015 M H^{+}$; ⊘, $0.030 M H^{+}$.

tion number (4 and 6, respectively) and that this provides a reason the second step proceeds the most slowly in the sequence of three. Likewise, the rate-determining step in the isotopic exchange reaction[21] between chromium(III) and -(VI) involves a similar coordination number change (provided these assignments of coordination number are correct). One instance has been noted, however, in which reaction of chromium(VI) with a 1-equiv. reducing agent does not follow this pattern. This is the oxidation of tris(1,10-phenanthroline)iron(II) ion,[3] in which the reaction of the complex with chromium(VI) is the slowest step. Only this species, of the ones yet examined, is required, by its known inertness to substitution, to react *via* an outer-sphere transition state. This has been taken as an indication that the other 1-equiv. reaction steps, in which reduction of chromium(V) (or oxidation of chromium(IV)) is relatively slow, may proceed through bridged transition states. This hypothesis must be regarded as tentative, although the known substitution lability of vanadium(IV) does not refute the idea with regard to the results of these kinetic studies.

The Rate Law Term Second Order in Chromium-(VI).—The path exhibiting second-order dependence upon $HCrO_4^{-}$ presumably involves $Cr_2O_7^{2-}$ as a reactant. This is analogous to the findings in the oxidation of aquoiron(II) ion by chromium(VI). In these cases of 1-equiv. reactions, unlike the situation in many 2-equiv. oxidations of organic substrates, the path involving $Cr_2O_7^{2-}$ contributes significantly. The transition state along this reaction pathway contains two chromium atoms and one vanadium, $(HCr_2O_7-V^{2+} \pm mH_2O)^{*}$. A mechanism consistent with these results is one similar to the reaction sequence 12-14, but involving $Cr_2O_7^{2-}$ as a reactant in the first step and a dimeric chromium(V)-(VI) species as the reaction intermediate in the rate-determining step.

Interpretation of the Induced Oxidation of Iodide Ion.—Many chromium(VI) oxidation-reduction reactions can induce the rapid oxidation of iodide ion under conditions where neither of the separate reactants or products can react rapidly. Westheimer[5] has discussed the significance of this effect, which has been attributed to a reactive intermediate formed during the course of the reaction. Such an intermediate which can oxidize iodide ion more rapidly than it can the substrate is largely diverted from the reaction sequence

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

normally followed had iodide ion been absent. According to the proposed mechanistic sequence B, reactions 12–14, this intermediate is chromium(V). The significance of the data previously presented on the change of F_i with the concentration ratio $[I^-]/[VO^{2+}]$ will be interpreted in terms of this mechanism.

The normal fate of chromium(V) is reaction with vanadium(IV) in reaction 13 at a specific rate k'_{45}. In the presence of iodide ion, another fate becomes possible for chromium(V), namely

$$Cr^V + I^- \longrightarrow Cr^{III} + HIO \ (k'_{I5}) \qquad (15)$$

$$I^- + HIO + H^+ = I_2 + H_2O \ (rapid) \qquad (16)$$
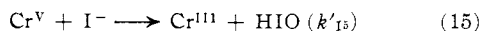
This scheme readily accounts for the change in F_i with the ratio $[I^-]/[VO^{2+}]$, for it is this ratio which determines the fraction of chromium(V) reacting along each of the alternative routes. Of the 3 equiv. of oxidizing power belonging to chromium(VI), vanadium(IV) always obtains one, in reaction 12. The remaining pair is divided between vanadium(IV), reactions 13 and 14, and iodide ion, reactions 15 and 16. The number of chromium(VI) oxidation equivalents used for iodide ion may not exceed two according to this mechanism, but it may approach this value as a limit at concentrations of iodide ion large relative to those of vanadium(IV).

The quantitative dependence of F_i upon concentrations of vanadium(IV) and iodide ions is derived from consideration of reactions 12–16. Reaction 12 oxidizes one vanadium(IV) for every chromium(VI) present, since the latter substance is present in quite insufficient amount. If x and y represent the concentrations of vanadium(IV) and iodide ion reacting by reactions 13 and 15, and C_{I_2} the formal concentration of iodine(0) at equilibrium, then

$$dx/dy = k'_{45}[VO^{2+}]/k'_{I5}[I^-] \cong x_{av}/y_{av} = x_{av}/2C_I$$

The ratio x/y is practically constant during each experiment, since the concentration ratio $[VO^{2+}]/[I^-]$ is relatively unchanged.

$$F_i = y/([Cr^{VI}]_0 + x) = 2C_{I_2}/[Cr^{VI}]_0 + x$$

Substitution and rearrangement lead to the result

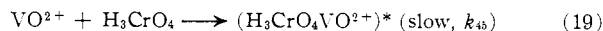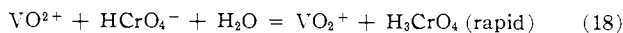$$F_i^{-1} - [Cr^{VI}]_0/2C_{I_2} = (k'_{45}/k'_{I5})([VO^{2+}]/[I^-])$$

The observed dependence upon $[H^+]$ requires modification of this equation

$$F_i^{-1} - [Cr^{VI}]_0/2C_{I_2} = (k_{45}/k_{I5})([VO^{2+}]/[I^-][H^+]) \qquad (17)$$

The results of these experiments agree quantitatively with eq. 17, as shown in Fig. 1. The slope of this plot gives $k_{45}/k_{I5} = 3.7 \times 10^{-4} \ M$. The mechanisms as written thus far have not taken into account any $[H^+]$ dependence. The role of hydrogen ions in these reactions will be taken up in the next section.

The Role of Hydrogen Ion in the Reaction Mechanisms.—The information provided by a kinetic study of the $[H^+]$ dependence of a reaction is limited to learning the *total* number of protons to be added to the predominant forms of the reactants in formation of the transition state. In the case of a mechanism consisting of a sequence of elementary reaction steps, such a study does not provide information concerning

the particular step(s) at which these hydrogen ions enter the sequence. For the path first order in chromium(VI) in the vanadium(IV)–chromium(VI) reaction, the observed lack of rate dependence upon $[H^+]$ allows more definitive conclusions to be drawn concerning this reaction and for some related reactions as well. Assuming that the observed hydrogen ion order is not due to a fortuitous cancellation, the elementary reaction sequence 12,13 can be written in terms of the dominant species
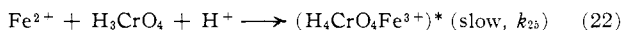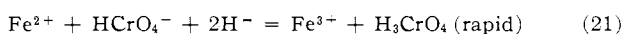
$$VO^{2+} + HCrO_4^- + H_2O = VO_2^+ + H_3CrO_4 \ (rapid) \qquad (18)$$

$$VO^{2+} + H_3CrO_4 \longrightarrow (H_3CrO_4VO^{2+})^* \ (slow, \ k_{45}) \qquad (19)$$

The formula written for chromium(V) is that consistent with coordination number 4; the formula H_3CrO_4 appears particularly reasonable since it is expected that chromium(V) is a weaker acid than chromium(VI).

The observation presented earlier that the rate constant ratio obtained from the experiments on the induced oxidation of iodide ion depends upon hydrogen ion indicates that the reaction of iodide ion and chromium(V) requires one additional proton

$$I^- + H^+ + H_3CrO_4 \longrightarrow (H_4CrO_4I)^* \ (k_{I5}) \qquad (20)$$
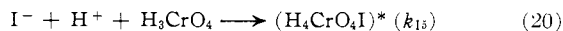
These conclusions can now be used in interpreting two earlier observations on the aquoiron(II)–chromium(VI) reaction.[3] In that system a rate law term is $k[Fe^{2+}]^2[HCrO_4^-][H^+]^3/[Fe^{3+}]$, and the rate constant ratio obtained from a study[22] of the induced oxidation of iodide is independent of $[H^+]$. The latter observation indicates that reaction of aquoiron(II) and chromium(V) requires the same number of added protons as does the iodide ion–chromium(V) reaction; this work establishes that number to be one. This enables the $[H^+]^3$ dependence to be understood as involving two protons in the prior equilibrium step and a single proton in the rate-determining step. A reaction sequence can now be written in terms of the dominant species indicating the steps at which hydrogen ions enter the sequence

$$Fe^{2+} + HCrO_4^- + 2H^- = Fe^{3+} + H_3CrO_4 \ (rapid) \qquad (21)$$

$$Fe^{2+} + H_3CrO_4 + H^+ \longrightarrow (H_4CrO_4Fe^{3+})^* \ (slow, \ k_{25}) \qquad (22)$$

Comparison with Other Results.—A suitable combination of these data and other information permits an interesting cross check on the results obtained for these reaction systems. The position of equilibrium in the reaction

$$Fe^{3+} + VO^{2+} + H_2O = Fe^{2+} + VO_2^+ + 2H^+ \qquad (23)$$
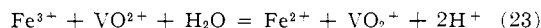
has been studied directly by a potentiometric technique[23]; at ionic strength $1.00 \ F$ and $25°$, the value of the equilibrium quotient $Q(23)$ is $1.5 \times 10^{-5} \ M^2$. Since reaction 23 is the algebraic difference of reactions 18 and 21, it is seen that the equilibrium quotient is related to known quantities. This work provides

$$Q(23) = \frac{Q(18)}{Q(21)} = \frac{(Q(18) \times k_{45})(k_{25}/k_{15})}{(Q(21) \times k_{25}) \ (k_{45}/k_{I5})} \qquad (24)$$

$Q(18)k_{45} = 0.56 \ M^{-1} \ sec.^{-1}$ and $k_{45}/k_{I5} = 3.7 \times 10^{-4} \ M$ at $25°$ and ionic strength $1.00 \ F$. Previous studies[3] have given $Q(21)k_{25} = 2.1 \times 10^8 \ M^{-4} \ sec.^{-1}$

(22) C. Wagner and W. Preiss, *Z. anorg. allgem. Chem.*, **168**, 265 (1928).
(23) J. Kenttamaa, *Suomen Khem.*, **21B**, 273 (1958).

at $0°$ and ionic strength $0.084\ F$. The data of Wagner and Preiss[22] lead to the result $k_{25}/k_{15} = 0.19$ at $0°$ and ionic strength $\sim 1.1\ F$ (chloride medium). Since these four parameters were not measured under the same conditions, the calculation indicated in eq. 24 can be only approximate. The value calculated is $1.4 \times 10^{-6}\ M^2$, compared with the experimental 15×10^{-6} M^2. Considering the variation in temperature and medium, these results appear not inconsistent. Especially gratifying is the observation that the concentration dependences of these four measured parameters are in not only apparent internal agreement, but that they combine to the correct form for the equilibrium quotient of reaction 23.

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The Oxidation of Oxalate Ion by Peroxodisulfate.
III. The Kinetics and Mechanism of the Catalysis by Silver(I)[1]

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The silver(I)-catalyzed oxidation of oxalate ion by peroxodisulfate has been studied. The rate law for this reaction in deaerated solution, at concentrations of peroxodisulfate greater than about $0.004\ M$, is $-\mathrm{d}[S_2O_8^{-2}]/\mathrm{d}t = k_1[S_2O_8^{-2}]^{3/2}[AgNO_3]^{1/2}$, with an activation energy of 16.4 kcal./mole. At peroxodisulfate concentrations of $0.004\ M$ or less, the rate law is $-\mathrm{d}[S_2O_8^{-2}]/\mathrm{d}t = k_{11}[S_2O_8^{-2}]^2$. In this concentration region a black precipitate forms during the reaction. It was identified by its X-ray diffraction pattern as metallic silver with traces of silver oxalate. A chain mechanism in which radical-ion chain carriers participate in one-electron-transfer reactions accounts for both rate laws (reactions 1–6). If the catalyst is present as the complex ion $AgC_2O_4^-$, rate laws of the same form are obtained. The effect of pH indicates that Ag^+ catalyzes the reaction at low pH, $AgC_2O_4^-$ at high pH. Oxygen inhibits the reaction. At partial pressures of oxygen between 2.9×10^{-5} and 1.31×10^{-3} atm., the rate law is $-\mathrm{d}[S_2O_8^{-2}]/\mathrm{d}t = k_{O_2}[S_2O_8^{-2}]^{3/2}[AgNO_3]^{1/2}/P^{1/2}$, with an activation energy of 22.4 kcal./mole. Inclusion of the additional reactions 19 and 20 in the mechanism leads to the observed rate law. The dissociation energy of $O_2CO_2^-$ is estimated to be approximately 8.2 kcal./mole.

The silver(I)-catalyzed oxidations of various substrates by peroxodisulfate are believed to be initiated by a reaction of silver(I) with peroxodisulfate ion.[3,4] The exact nature of this reaction is not clear although a one-electron oxidation

$$Ag^+ + S_2O_8^{-2} \longrightarrow Ag^{+2} + SO_4^- + SO_4^{-2} \qquad (1)$$
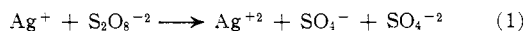
is in accord with the experimental evidence.[3,4]

Reaction 1 appears to be rate-determining in the silver(I)-catalyzed oxidations of most substrates.[3,4] In this respect, the oxidation of oxalate ion is exceptional. King[5] found that, in partially deaerated solutions, this reaction was about 4000 times as fast as the oxidations of other substrates under similar conditions. The erratic nature of his results precluded a quantitative kinetic investigation.

Later it was shown that, in solutions of very low copper concentration but not deaerated, the silver(I)-catalyzed oxidation of oxalate is only slightly faster than the oxidations of other substrates.[6]

The catalytic properties of copper and the inhibitory nature of oxygen in the oxidation of oxalate ion have been confirmed in a recent study.[7] For the copper-(II)-catalyzed reaction the experimental rate law

$$-\mathrm{d}[S_2O_8^{-2}]/\mathrm{d}t = k[S_2O_8^{-2}][Cu^{II}(C_2O_4)_2^{-2}]^{1/2}$$

is consistent with a chain mechanism involving the radical ions CO_2^- and SO_4^- and oxidation of copper to

the tervalent state. Inhibition by oxygen occurs through reaction with CO_2^- radicals followed by chain termination.

As silver(I) is susceptible to one-electron oxidation to the unstable silver(II), it can play a role similar to that of copper(II) in catalyzing propagation. It can also initiate chains by reaction 1. Therefore, silver(I) should be at least as effective a catalyst as copper(II).

The present kinetic investigation was undertaken to uncover the mechanism of the silver(I)-catalyzed oxidation of oxalate ion by peroxodisulfate.

Experimental

Materials.—Water was purified by distillation through a 36-in. Vigreux column equipped with an electric heating tape at the takeoff to prevent diffusion of impurities into the distillate.[8] The distillate was collected and stored in polyethylene bottles.

National Bureau of Standards standard sodium oxalate (batch No. 40g), Mallinckrodt analytical reagent grade potassium peroxodisulfate, silver nitrate, and cupric sulfate, and Baker and Adamson reagent grade anhydrous sodium sulfate were used without further purification. Gases used were Matheson helium and Liquid Carbonic Industrial oxygen.

Baker and Adamson reagent grade concentrated sulfuric acid was redistilled in an all-Pyrex apparatus and stored in a ground-glass-stoppered Pyrex flask. Eastman Kodak (White Label) allyl acetate was fractionally distilled through a 15-cm. column packed with glass helices shortly before use. A fraction boiling at $103°$ was used.

Reaction mixtures were made from standard stock solutions in most of the experiments. These were prepared with redistilled water and stored in polyethylene bottles. All pipets and other glassware were Pyrex glass and were thoroughly washed with redistilled hydrochloric acid and redistilled water as a precaution against metal contamination.

Apparatus.—Since oxygen is a powerful inhibitor of the silver(I)-catalyzed reaction, the reaction vessel was a Pyrex gas-washing bottle with a fritted disk (flask I) to facilitate deaeration of reaction mixtures by flushing with helium. A 21.0-ml. pipet, equipped with a ground-glass joint fitting snugly into the cover of the reaction vessel, was used for sampling. Aliquots could

(1) Abstracted in part from the Ph.D. Dissertation of A. Joseph Kalb, University of California, Davis, Calif., 1963, presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963.

(2) Public Health Service Predoctoral Fellow, 1962–1963.

(3) W. K. Wilmarth and A. Haim in "Peroxide Reaction Mechanisms, Conference, Providence, Rhode Island, 1960," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, p. 175.

(4) D. A. House, Chem. Rev., 62, 185 (1962).

(5) C. V. King, J. Am. Chem. Soc., 50, 2089 (1928).

(6) T. L. Allen, ibid., 73, 3589 (1951).

(7) E. Ben-Zvi and T. L. Allen, ibid., 83, 4352 (1961).

(8) R. Ballentine, Anal. Chem., 26, 549 (1954).