presence of H^+ and IO_3^- at suitable concentrations? It has long been clear that the reduction of IO_3^- by H_2O_2 to give iodine[13] begins this induction period and continues throughout the decomposition, whether oscillating or smooth.

The oscillating decomposition is characterized by a pulsating evolution of oxygen, for which a peak rate near 1.6 × 10^{-2} mol/(l. min) has been measured.[14] So long as $[H_2O_2]$ is appreciable, this peak rate is many times the rate of the Dushman reaction calculated from eq 2a for the concentration existing in the H_2O_2 system. But, the latter rate is comparable with the rate of iodine formation that can result from the reduction of IO_3^- by H_2O_2. For this reduction at 50°, the rate law is[13]

$$+d[I_2]/dt = -{}^1/_2 d[IO_3^-]/dt = 2.6 \times 10^{-4}[IO_3^-][H_2O_2] + 129 \times 10^{-4}[H^+][IO_3^-][H_2O_2] \quad (20)$$

By equating this rate of iodine formation to that calculated from eq 2a, one obtains the (I^-) at which the two rates are equal. At 50°, the mean k_2' is near 29 × 10^4. For $[H_2O_2] = 0.5$, $[IO_3^-] = 0.1$, and $[H^+] = 0.1$, equality exists when (I^-) is near 9×10^{-8}. This is a reasonable value for (I^-) during the oscillating decomposition.[14] The Dushman reaction may well be involved. If that is true, then the Dushman reaction *will also oscillate*, for it is coupled to the decomposition *via* (I^-), which shows pronounced oscillations.[14] We could then have a situation in which an oscillating formation of iodine *via* the Dushman reaction is superimposed on a steady formation of iodine *via* the reduction of iodate by hydrogen peroxide. Such a situation could obviously influence the pulsating oxygen evolution.

Acknowledgment.—We thank the Robert A. Welch Foundation for supporting this work.

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[13] H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **53**, 896 (1931).

[14] I. Matsuzaki, R. B. Alexander, and H. A. Liebhafsky, *Anal. Chem.*, **42**, 1690 (1970); note Figure 7.

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The Oxidation of Uranium(IV) by Chromium(VI) and the Induced Oxidation of Iodide Ions[1a]

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The oxidation of U(IV) by Cr(VI) proceeds quantitatively to UO_2^{2+} and $Cr(H_2O)_6^{3+}$. A stopped-flow kinetic study was carried out; after allowance for acid dissociation reactions, the rate equation is $-d[Cr(VI)]/dt = \{k' + k[H^+]^{-1}\}[U^{4+}] \cdot [HCrO_4^-]$, where the acid-independent term, which is quite small, probably represents a medium effect. The reaction produces Cr(V) as an intermediate, as evidenced by the induced oxidation of iodide ions. The iodine yield was evaluated as a function of $[I^-]/[U^{4+}]$ and $[H^+]$ and indicates U(V) is not an intermediate, which is also supported by the effect of Fe^{3+} as well as by ^{18}O studies in the literature. Some experiments on the reactions of U(III) and U(V) with Cr(VI) are also reported.

Introduction

The oxidation of U(IV) by Cr(VI), eq 1, constitutes

$$3U^{4+} + 2HCrO_4^- + 2H^+ = 3UO_2^{2+} + 2Cr^{3+} + 2H_2O \quad (1)$$

a standard volumetric analysis for uranium.[2] Rao, *et al.*,[3] reported that the oxidation occurs rapidly, any apparent slowness being attributable to a sluggish indicator reaction.

We found no indications that earlier kinetic studies had been made, presumably owing to the high reaction rate. The reaction of U(IV) and Cr(VI) induces the oxidation of iodide ions,[4,5] but the reported yields of iodine could be rationalized only by an involved sequence of reactions with a particular coincidence of rates.[6] The oxygen-18 study of Gordon and Taube[7] disclosed appreciable oxygen transfer from Cr(VI) to UO_2^{2+}.

We present here the results of a detailed kinetic study carried out in perchlorate solution, as a function of hydrogen ion concentration and temperature. The induced oxidation of iodide was also studied under the same controlled conditions, with results in good accord with a reasonable reaction mechanism. The roles of possible reaction intermediates, particularly Cr(V) and U(V), were studied, by consideration of the iodide experiments, by studying a possible rate effect of Fe(III), by considering the implications of the ^{18}O experiments, and by a direct but cursory examination of the U(V)–Cr(VI) reaction.

Experimental Section

Materials.—Uranyl(VI) perchlorate was prepared by heating U_3O_8 in perchloric acid and crystallizing $UO_2(ClO_4)_2 \cdot XH_2O$. Reduction of the acidified aqueous solutions to U(IV) was accomplished with amalgamated zinc, followed by air oxidation of any U(III) produced. The U(IV) solutions were analyzed by cerium(IV) titration and/or by spectrophotometry.

Solutions of U(V) were prepared by the reaction of europium(II) with uranium(VI) at low acidity.[8] Other reagents were prepared as before.[9a,10]

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[1] Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 3117. (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

[2] I. M. Kolthoff and J. J. Lingane, *J. Amer. Chem. Soc.*, **55**, 1871 (1933).

[3] V. P. Rao, B. V. S. R. Murty, and G. G. Rao, *Z. Anal. Chem.*, **147**, 199 (1955).

[4] W. Manchot, *Ber.*, **39**, 1352, 3510 (1906).

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

[6] F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

[7] G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962).

[8] T. W. Newton and F. B. Baker, *ibid.*, **4**, 1166 (1965).

[9] (a) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 5101 (1964). (b) As pointed out to the authors by T. W. Newton the left-hand side of eq 24 is equivalent to the simpler expression $(F^{-1} + 1)/3$.

[10] J. H. Espenson and R. J. Kinney, *Inorg. Chem.*, **10**, 376 (1971).

Rate Measurements.—The reaction rate proved measurable only at relatively high acidities.[11] A stopped-flow instrument using spectrophotometric detection (Durrum Instrument Co.) was employed for the rate studies, using a mixing chamber constructed of Kel-F with a cuvette having a 2-cm optical path. Most of the experiments were carried out at λ 350 nm where Cr(VI), present largely as $HCrO_4^-$ and H_2CrO_4 under the conditions employed, makes the only appreciable contribution to the absorbance.

The solutions were maintained at a relatively high ionic strength, 3.00 *M*, to permit a wide range of $[H^+]$ variation. Lithium perchlorate was used to control the ionic strength.

Uranium(IV) was present in excess in every experiment, often in sufficient excess ($[U^{4+}]_0/[Cr(VI)]_0 \geq 15$) that $[U^{4+}]$ was approximately constant during the run. In such cases a first-order rate plot was constructed and found to be linear to $\geq 80\%$ completion. A second-order rate constant was computed by dividing the pseudo-first-order rate constant by the average U(IV) concentration in the run. In runs in which the concentration ratio was not as large, the second-order rate plot appropriate to the rate law in eq 2 was made; such plots were also linear and gave

$$-d[Cr(VI)]/dt = k_2'[U(IV)][Cr(VI)] \qquad (2)$$

second-order rate constants consistent with the values derived from the pseudo-first-order experiments.

Stoichiometry Experiments.—The stoichiometry as given in eq 1 is well established from its use as a method for U(IV) analysis. To confirm that the same equation applied under the conditions of the kinetic determinations, two sets of experiments were performed. First, solutions of U(IV) were treated with excess Cr(VI), and the excess was determined spectrophotometrically. The average of five determinations gave 1.48 ± 0.07 mol of U(IV) consumed per mole of Cr(VI) reacted. Second, a solution of U(IV) was treated with successive 20-μl portions of a concentrated Cr(VI) solution, and the spectrum was scanned between 300 and 700 nm after each addition. A total of six isosbestic points was noted, which remained unchanged with successive additions until the added quantity of Cr(VI) exceeded the stoichiometric amount. We interpret this to mean that no intermediates accumulate in the presence of excess U(IV), because the concentrations of the reactants and products are changing by identical amounts.

Induced Oxidation of Iodide.—The yield of iodine was determined at its absorption maximum at λ 465 nm. The apparent molar absorptivity of iodine is somewhat dependent upon $[I^-]$, owing to I_3^- formation. A simple calibration of ϵ_{app} as a function of $[I^-]$ was made; the values lay between 717 M^{-1} cm^{-1} at 8.2×10^{-4} *M* I^- and 755 M^{-1} cm^{-1} at 9.2×10^{-3} *M* I^-.

The reaction between U(IV) and I_2 was first presumed to be slow, because the bromine oxidation occurs quite slowly;[12] this was confirmed directly to ensure that the measured yield of iodine would not be affected.

Results

Kinetics.—The reaction rate was measured as a function of the concentration variables over the following ranges of initial concentration: $(2.3–31) \times 10^{-4}$ *F* U(IV), $(1.7–4.1) \times 10^{-5}$ *F* Cr(VI), and 0.15–3.0 *M* H^+. The apparent second-order rate constant, k_2' of eq 2, is independent of [U(IV)] and [Cr(VI)] at any particular $[H^+]$. Table I summarizes the average value of k_2' at each $[H^+]$ studied.

Expressing the rate law in terms of the concentration of U^{4+} and $HCrO_4^-$, which are the predominant species under these conditions

$$-d[Cr(VI)]/dt = k_2[U^{4+}][HCrO_4^-] \qquad (3)$$

where the rate constant k_2 may depend upon $[H^+]$. Allowance must be made for the acid–base equilibria

$$U_{aq}^{4+} + H_2O \rightleftharpoons H^+ + UOH^{3+} \qquad K_U = 0.010\ M^{13} \qquad (4)$$

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \qquad K_{Cr} = 5.0\ M^{14,15} \qquad (5)$$

Consideration of these two equilibria results in

$$k_2 = k_2'\left(\frac{[H^+] + K_U}{[H^+]}\right)\left(\frac{[H^+] + K_{Cr}}{K_{Cr}}\right) \qquad (6)$$

eq 6. Also summarized in Table I are the average values of k_2 at each acid concentration.

TABLE I

RATE CONSTANTS AS A FUNCTION OF HYDROGEN ION CONCENTRATION (25.0°, μ = 3.0 *M*)

$[H^+]$, *M*	$10^{-4}k_2'$, M^{-1} sec^{-1}	$10^{-4}k_2$,[a] M^{-1} sec^{-1}	$[H^+]$, *M*	$10^{-4}k_2'$, M^{-1} sec^{-1}	$10^{-4}k_2$,[a] M^{-1} sec^{-1}
2.99	1.94	3.11	0.890	5.73	6.83
2.65	2.12	3.26	0.650	8.3	9.52
2.60	2.07	3.16	0.500	9.8	11.0
2.44	2.32	3.47	0.400	13.5	14.9
2.25	2.28	3.32	0.300	17.6	19.3
2.00	3.03	4.26	0.250	21.6	23.6
1.50	3.29	4.31	0.200	27.5	30.0
1.00	5.20	6.30	0.150	37.5	41.2

[a] Corrected for the acid dissociation equilibria of eq 4 and 5 by the relation given in eq 6.

A plot of k_2 *vs.* $1/[H^+]$ is linear, as shown in Figure 1.

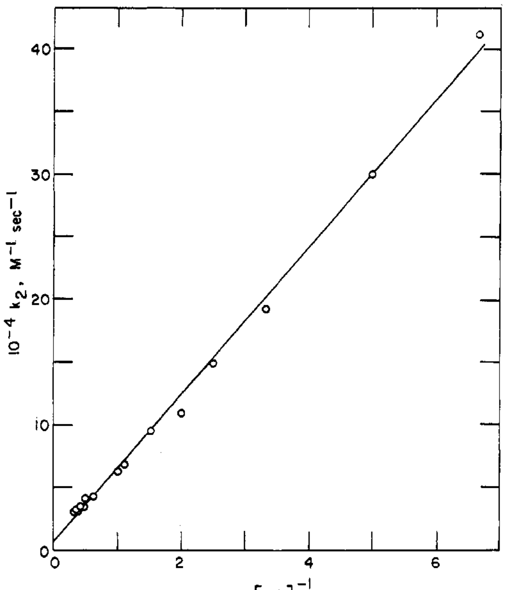

Figure 1.—A plot of the apparent second-order rate constant, after correction for the acid–base equilibria, *vs.* $[H^+]^{-1}$.

The intercept is small, but nonzero, in accord with the rate law in eq 7. A least-squares fit of the data in

$$-d[Cr(VI)]/dt = \{k' + k[H^+]^{-1}\}[U^{4+}][HCrO_4^-] \qquad (7)$$

Table I was made[16] resulting in the values $k' = (0.57 \pm 0.24) \times 10^4$ M^{-1} sec^{-1} and $k = (5.89 \pm 0.09) \times 10^4$ sec^{-1} at 25.0° and μ = 3.00 *M*. The value of the intercept is quite small; it may correspond to a genuine, albeit minor, reaction pathway or merely to a medium effect. The mechanism will be considered further in the Discussion.

The Induced Oxidation of Iodide.—A quantitative

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[11] Preliminary experiments by F. B. Baker and T. W. Newton indicated that the reaction would occur at a measurable rate in solutions of relatively high $[H^+]$.

[12] G. Gordon and A. Andrews, *Inorg. Chem.*, **3**, 1733 (1964).

[13] S. Hietanen, *Acta Chem. Scand.*, **10**, 1531 (1956); *Recl. Trav. Chim. Pays-Bas*, **75**, 711 (1956).

[14] (a) G. P. Haight, Jr., D. C. Henderson, and N. H. Coburn, *Inorg. Chem.*, **3**, 1804 (1964); (b) J. Y. Tong, *ibid.*, **3**, 1804 (1964), concurred with a higher value of K_{Cr} than originally reported.[15]

[15] J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **75**, 6180 (1953).

[16] The computer program was based upon Report LA-2367 from Los Alamos Scientific Laboratory; we are grateful to Drs. T. W. Newton and R. H. Moore for supplying copies of the program.

study was made of the yield of iodine produced, relative to that of U(VI), when mixtures of I^- and U(IV) of varying composition were oxidized by Cr(VI). To simplify the interpretation of the data obtained, only a small amount of Cr(VI) was added, such that the amounts of U(IV) and I^- oxidized were only a small part of the total; consequently the ratio $[U(IV)]/[I^-]$ remained nearly constant in any experiment.

The difference between the number of equivalents of Cr(VI) added and the number of equivalents of iodine produced yields the net number of equivalents of U(IV) oxidized. These results are expressed in terms of the *induction factor*, F_i, defined by eq 8.

$$F_i = \Delta(\text{equiv of I}^-)/\Delta(\text{equiv of U}^{IV}) \qquad (8)$$

Figure 2 illustrates the data obtained by a plot of F_i *vs.* the concentration ratio $[I^-]/[U(IV)]$. It is evident from these data that the induction factor increases with the concentration ratio, reaching a limiting value of 2.0; moreover, the rate of change of F_i with $[I^-]/[U(IV)]$ increases with $[H^+]$.

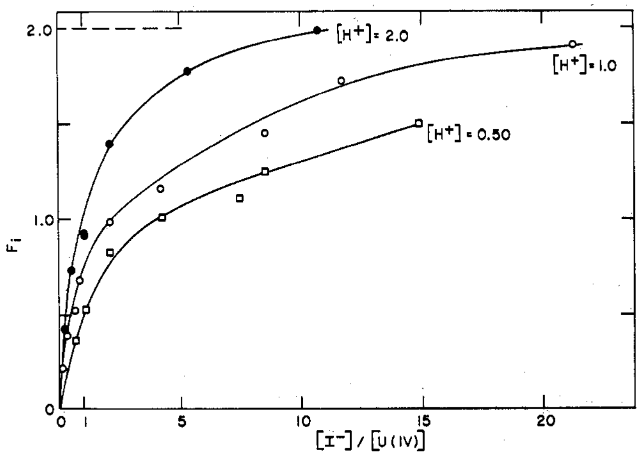

Figure 2.—A plot of the induction factor, F_i, defined by eq 8, *vs.* $[I^-]/[U^{4+}]$ at different $[H^+]$ values.

The quantitative interpretation of these results lies in the competing reductions of Cr(V) by U(IV) and I^-. The limiting value of F_i at high values of the concentration ratio leads to the stoichiometric equation given by eq 9, which is applicable only in the indicated con-

$$2Cr(VI) + U(IV) + 4I^- = 2Cr(III) + U(VI) + 2I_2 \qquad (9)$$

centration limit. A more quantitative interpretation of these results will be offered in the Discussion.

The Effect of Fe(III).—Kinetics experiments were performed to examine the effect of fairly high concentrations of Fe^{3+}. Owing to the fairly rapid reaction between U^{4+} and Fe^{3+},[17] these measurements were carried out with the iron(III) mixed with chromium(VI) in one reservoir syringe of the stopped-flow apparatus and uranium(IV) in the other. Even with excess U(IV) and 10^{-2} *M* Fe(III), the U(IV)–Fe(III) reaction was slow enough to be unimportant during the time required for complete reduction of Cr(VI).

On the other hand, the reduction of Fe(III) by U(V), should the latter be formed, is necessarily[17] a rapid reaction; Newton and Baker[18] estimated a second-order rate constant of 2.5×10^5 M^{-1} sec^{-1} at 25° with $[H^+] = 1$ *M* and $\mu = 2$ *M*. The purpose of this experiment is to provide evidence, by the effect of Fe(III), or lack thereof, for the production of U(V).

The runs with added Fe(III) proved to proceed identically, in the limits of experimental error, with runs in which Fe(III) was not present. For example, a run at $[H^+] = 0.500$ *M* having $[Fe^{3+}] = 0.011$ *M* and $[U^{4+}]_0 = 6.7 \times 10^{-4}$ *M* had $10^{-4} k_2' = 9.4$ M^{-1} sec^{-1}, compared to 9.8 M^{-1} sec^{-1} in its absence. Again, these results will be accounted for by the mechanism subsequently presented.

Temperature Studies.—The reaction rate was measured at a total of five temperatures in the range 10.0–34.1°. The experiments were carried out at 1.00 *M* H^+, where both the hydrolysis equilibria, eq 4 and 5, are relatively unimportant, so that corrections need not be applied, and where the $[H^+]^{-1}$ term of eq 7 predominates.

The activation parameters corresponding to k of eq 7 and their standard deviations are $\Delta H^{\ddagger} = 13.3 \pm 1.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = 7.9 \pm 4.8$ cal mol^{-1} deg^{-1}; in terms of the mechanism subsequently presented, $\Delta S^{\ddagger}$ for the rate-determining step would be larger by $R \ln 2$ (1.4 eu).

Experiments on U(V).—Some attempts were made to study directly the reaction of U(V) and Cr(VI), eq 10,

$$3U(V) + Cr(VI) = 3U(VI) + Cr(III) \qquad (10)$$

because this would be an important process in the U(VI) reaction if U(V) were produced.

These experiments are difficult, because the disproportionation of U(V), eq 11, occurs fairly rapidly even

$$2U(V) = U(IV) + U(VI) \qquad (11)$$

at low $[H^+]$.

The experiments were carried out by generating U(V) at 0.02 *M* H^+ and mixing this solution with acidified Cr(VI) to give a final $[H^+]$ of 0.5 *M*. These experiments did lead to the reduction of Cr(VI). Moreover, the reaction occurred too rapidly to be attributed to the reduction of Cr(VI) by any U(IV) formed in reaction 11. The concentrations are, however, difficult to control; assuming the rate of reaction 10 is given by the expression

$$-d[Cr(VI)]/dt = k_{10}[U(V)][Cr(VI)] \qquad (12)$$

we estimate a value $k_{10} \approx 1.3 \times 10^5$ M^{-1} sec^{-1} at 25.0°, 0.50 *M* H^+, and $\mu = 3.0$ *M*.

Experiments on U(III).—Several attempts were made, both at high and low $[H^+]$, to evaluate the rate of oxidation of U^{3+} by Cr(VI). With excess U^{3+} an absorbance decrease at λ 350 nm was noted, but this proved to be the reaction of U^{3+} and UO_2^{2+}, as studied by Newton and Fulton.[19] The reaction between U(III) and Cr(VI) apparently occurs too rapidly for us to measure using the stopped-flow method under all conditions tried.

Interpretation and Discussion

1- *vs.* 2-Equivalent Mechanisms.—The oxidation of U(IV) appears to proceed without the intermediate production of U(V). The following observations form the basis on which we conclude U(V) is probably not an important intermediate. First, the oxidation of U(V) by Cr(VI) is faster than that of U(IV) but probably

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[17] R. H. Betts, *Can. J. Chem.*, **33**, 1780 (1955).

[18] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **70**, 1943 (1966).

[19] T. W. Newton and R. B. Fulton, *ibid.*, **74**, 2797 (1970).

not so fast to maintain the observed pseudo-first-order dependence on Cr(VI). Hence either U(V) is not formed at substantial concentrations or it disappears by a reaction more rapid than that with Cr(VI). Second, the rapid reaction[17,18] of U(V) and Fe(III), eq 13, would be sufficient to divert a considerable

$$\mathrm{U(V) + Fe(III) \longrightarrow U(VI) + Fe(II)} \qquad (13)$$

proportion of the U(V), were it formed, in preference to its oxidation by Cr(V). The lack of Fe(III) effect on the rate of Cr(VI) disappearance argues that U(V) is not produced; otherwise, reaction 13 would occur in preference to reaction 10 or other known U(V)-consuming processes, resulting in a considerable lowering of the rate with added Fe(III).[20] Finally, Gordon and Taube[21] have shown that U(V) is a powerful catalyst for the exchange of oxygen between U(VI) and water. Because they noted a remarkable degree of oxygen transfer from ^{18}O experiments in the present reaction[7] (carried out, however, at concentrations much higher than in the kinetic studies), the absence of an appreciable concentration of U(V) is indicated.

For these reasons we are led to conclude that U(V) is not an important intermediate; either the reaction occurs by 2-equiv steps wherein U(V) is never produced or there are reactions leading to its destruction which occur more rapidly than the ones considered above.

Proposed Reaction Mechanism.—The following mechanism, with $k = 2k_{14}$, is consistent with all the stoichiometric and kinetic data presented

$$\mathrm{U(IV) + Cr(VI) \longrightarrow U(VI) + Cr(IV)} \qquad (14)$$

$$\mathrm{Cr(IV) + Cr(VI) = 2Cr(V)} \quad \text{(fast)} \qquad (15)$$

$$\mathrm{Cr(V) + U(IV) = Cr(III) + U(VI)} \quad \text{(fast)} \qquad (16)$$

The hydrogen ion dependence of the rate-determining step is in accord with the net activation process

$$\mathrm{U^{4+} + HCrO_4^- = [UCrO_4 \pm \mathit{n}H_2O^{2+}]^{\ddagger} + H^+} \qquad (17)$$

which avoids raising the question of whether the reaction occurs between U^{4+} and CrO_4^{2-} or UOH^{3+} and $HCrO_4^-$ (among other possibilities).

In addition to this process, which is the main pathway for reaction 14, there is a small hydrogen ion independent rate term. This might represent the contribution corresponding either to a transition state containing one proton more than that shown in eq 17 or to an artifact resulting from the imperfect control of all activity coefficients by the maintenance of constant ionic stregnth. To test the latter possibility, a method used many times before[22] was tried: are the rate constants adequately accounted for by the following expression, rather than by eq 7

$$k_2 = k^0[\mathrm{H^+}]^{-1}\exp(-\beta[\mathrm{H^+}]) \qquad (18)$$

where k^0 is the intrinsic rate constant, applicable to the idealized situation where all the activity coefficients remain at the values appropriate to 3.00 F $LiClO_4$, and the exponential term represents a correction for the fact they do not? The small correction is made in a manner consistent with the observations of Harned[23,24] for mixed electrolytes. This treatment gives $k^0 = 5.89 \pm 0.09 \times 10^{-4}$ sec^{-1} and $\beta = -0.10 \pm 0.01$ M^{-1}. The value of β is reasonably small, within the range where the intercept shown in Figure 1 may well be due to such an effect. Consequently, we cannot state whether the [H$^+$]-independent part of eq 7 is to be attributed to a minor but authentic reaction pathway or to a small but significant medium effect. Certainly, the data do not provide clear evidence for a transition state $[\mathrm{UHCrO_4}^{3+}]^{\ddagger}$.

The Role of Cr(V).—The effect of iodide ions is to act as scanvenger[6,9,25,26] for Cr(V), competing with reaction 16

$$\mathrm{Cr(V) + I^- + H^+ \longrightarrow Cr(III) + HOI} \qquad (19)$$

$$\mathrm{HOI + I^- \longrightarrow I_2} \qquad (20)$$

$$\mathrm{Cr(V) + 2I^- = Cr(III) + I_2} \qquad (21)$$

The sum of reactions 14,15, and 21 leads to an equation in accord with eq 9, corresponding to the limiting stoichiometry at high [I$^-$]/[U(IV)] ratios.

More quantitatively, the variation of F_i with [I$^-$]/[U^{4+}] and with [H$^+$] can be accounted for by reactions 14–16 and 19–21 by the following development.[9]

Reactions 14 and 15 oxidize 0.50 mol (1.0 equiv) of U(IV) for every mole of Cr(VI) added, since the latter is present in relatively small concentration and since, from the form of the reaction kinetics, $R_{15} \gg R_{14}$ (R = rate). If x and y represent the molar concentrations of U(IV) and iodide ions reacting by reactions 16, 19, and 20, respectively, then

$$\mathrm{d}x/\mathrm{d}y \cong x_{\mathrm{av}}/y_{\mathrm{av}} = k_{16}[\mathrm{U(IV)}][\mathrm{H^+}]^n/k_{19}[\mathrm{I^-}][\mathrm{H^+}] \qquad (22)$$

where n is the order of reaction 16 with respect to [H$^+$], and x/y is practically constant because the ratio [U(IV)]/[I$^-$] is relatively unchanged. The consumption of y M I$^-$ by reactions 19 and 20 leads to the production of $(y/2)$ M I_2; $C_{I_2} = y/2$. The consumption of I$^-$ thus corresponds to $2C_{I_2}$ equiv, and that of U(IV) is $2\{{}^1/_2[\mathrm{Cr(VI)}]_0 + x\}$ equiv leading to

$$F_1 = C_{\mathrm{I_2}}/\{{}^1/_2[\mathrm{Cr(VI)}]_0 + x\} \qquad (23)$$

Combination of eq 22 and 23 gives the result[9b]

$$F_i^{-1} - [\mathrm{Cr(VI)}]_0/2C_{\mathrm{I_2}} = (k_{16}/k_{19})\{[\mathrm{U^{4+}}][\mathrm{I^-}]^{-1}[\mathrm{H^+}]^{n-1}\} \qquad (24)$$

Figure 3 shows a plot of the left-hand side of eq 24 *vs.* $[\mathrm{U^{4+}}][\mathrm{I^-}]^{-1}[\mathrm{H^+}]^{-1}$; the value $n = 0$ was chosen to yield a linear plot.

The rate of eq 16 is thus given by the equation

$$-\mathrm{d}[\mathrm{Cr(V)}]/\mathrm{d}t = k_{16}[\mathrm{U^{4+}}][\mathrm{H_3CrO_4}] \qquad (25)$$

with a rate constant, relative to reaction 19, given by $k_{16}/k_{19} = 0.59$ M^{-1}.

Wetton and Higginson[27] raised a general objection

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[20] As pointed out to the authors by T. W. Newton (private communication), the Fe(III) experiments alone are not sufficient evidence to rule out the production of U(V), because the logical sequence given above is dependent upon other possible intervening reactions whose rates might not be known. For example, were reaction 13 followed by two reactions

$$\mathrm{Fe(II) + Cr(VI) \longrightarrow Fe(III) + Cr(V)} \qquad (13a)$$

$$\mathrm{Cr(V) + U(IV) \longrightarrow Cr(III) + U(VI)} \qquad (13b)$$

and if these were both more rapid than eq 13, then Fe(III) would show no kinetic effect on the main reaction even if the products of the rate-determining step were U(V) + Cr(V).

[21] G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **16**, 272 (1961).

[22] O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 1313 (1969).

[23] H. S. Harned, *ibid.*, **48**, 326 (1926).

[24] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, Chapter 15.

[25] J. H. Espenson, *Accounts Chem. Res.*, **3**, 347 (1970).

[26] (a) K. M. Davies and J. H. Espenson, *J. Amer. Chem. Soc.*, **92**, 1884 (1970); (b) *ibid.*, **92**, 1885 (1970). (c) Note that reaction 16 has a first-order dependence on [H$^+$].

[27] E. A. M. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 5890 (1965).

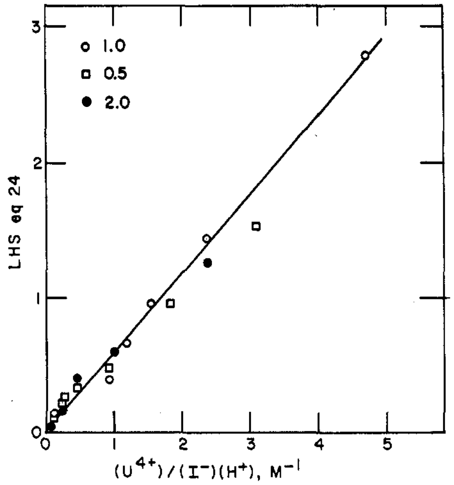
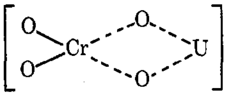


Figure 3.—A plot relating the induction factor, measured under all concentration conditions, to concentration variables, in accord with eq 24 for $n = 0$.

to the inclusion of the Cr(IV) + Cr(VI) reaction shown in reaction 15, because their estimates (which contain considerable uncertainties) indicate that the equilibrium constant is less than unity. More complicated sequences, for example, the production of a Cr^{III}–U^{V} dinuclear species, could be written as alternative rapid steps.

Detailed Mechanism.—The published oxygen-18 studies[12] on U(IV) oxidation lead to the result that for both $HCrO_4^-$ and MnO_4^- the extent of oxygen transfer can exceed 1 oxygen per UO_2^{2+} transferred from the oxidizing agent (Cr(VI), 0.9–1.2; Mn(VII), 1.1–1.7), as can the number of oxygen atoms in UO_2^{2+} derived per one molecule of the oxidizing agent (Cr(VI), 1.3–1.8; Mn(VII), 3.5–4.0). In the case of MnO_4^-, the authors propose a doubly bridged transition state resulting in the simultaneous transfer of 2 oxygen atoms. The Cr(IV) result requires that the rate of oxygen exchange of Cr(IV) and/or Cr(V) with the solvent be slower than the rate of U(V) oxidation. A mechanism analogous to that originally proposed for MnO_4^- + U(IV) seems plausible[28] in this instance also, although the resulting UO_2 group would be badly distorted from linearity



This suggestion or any other that is to account for the observed extent of oxygen transfer must (a) involve prior complexation of Cr(VI) and U(IV) and (b) produce U(VI) more rapidly than the oxygen exchange of Cr(VI) and water, itself a rapid reaction,[29] especially at high hydrogen ion concentrations. Complexation of Cr(VI) as CrO_4^{2-} has been observed, for example, by Ce(IV),[30] Co(III),[31] Fe(III),[32] and Np(IV).[33] In the present study, the reactant concentrations were so low and the hydrogen ion concentration was so high that an equilibrium

$$U^{4+} + HCrO_4^- \rightleftarrows UCrO_4^{2+} + H^+ \qquad (26)$$

would be displaced so far to the left that it would not cause appreciable deviations from second-order kinetics, even if its stability were as high as the most stable of the Cr(VI) complexes cited above, that with Np(IV). The apparent nonaccumulation of a substantial concentration of the $UCrO_4^{2+}$ complex is in accord with our observation that the apparent second-order rate constants were not dependent upon the reactant concentrations at constant $[H^+]$.

The suggestion that reaction 14 proceeds by way of the complex formed in an equilibrium such as eq 26 remains an attractive one, however; the oxygen-18 experiment is accounted for, at least qualitatively, and the composition[33] of the complex corresponds to that of the transition state for reaction 14.

Generally, Cr(VI) oxidations of metal ions are uninfluenced or accelerated by increasing $[H^+]$; the oxidation of U(IV), Np(IV),[34a] and Pu(IV)[34b] by Cr(VI) appears unique in this respect. The effect arises largely because here an aquo ion, U_{aq}^{4+}, is oxidized directly to an oxo ion, UO_2^{2+}, resulting in the net process

$$U^{4+} + HCrO_4^- + 4H_2O \longrightarrow UO_2^{2+} + Cr(OH)_4(H_2O)_2 + H^+ \qquad (27)$$

where the H^+ produced is removed from one reactant prior to formation of the transition state.

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[28] We are grateful to Professor Richard C. Thompson for this suggestion.

[29] (a) R. H. Holyen and H. W. Baldwin, *Can. J. Chem.*, **45**, 413 (1967); (b) J. R. Pladziewicz and J. H. Espenson, *Inorg. Chem.*, **10**, 634 (1971).

[30] J. Y. Tong and E. L. King, *J. Amer. Chem. Soc.*, **76**, 2132 (1954).

[31] J. C. Sullivan and J. E. French, *Inorg. Chem.*, **3**, 832 (1964).

[32] (a) J. H. Espenson and E. L. King, *J. Amer. Chem. Soc.*, **85**, 3328 (1963); (b) J. H. Espenson and S. R. Helzer, *Inorg. Chem.*, **8**, 1051 (1969).

[33] R. L. Thompson, private communication, noted the formation of $NpCrO_4^{2+}$.

[34] (a) R. C. Thompson and M. J. Burkhart, private communications; (b) R. E. Connick in "The Actinide Elements," G. T. Seaborg and J. J. Katz, Ed., McGraw-Hill, New York, N. Y., 1954, p 261.