exponential factor μ and n is the principal quantum number for the atomic orbital, eq. 1 simplifies as follows for the transitions of $[\mathrm{MoOCl_5}]^{2-}$

A. $^2B_2 \longrightarrow {}^2E(I)$, f = 1.085 ×

$$10^{-5}\,(\nu_{\mathrm{cm}^{-1}})\left[\frac{[N_{2p}c_2{}^{e\pi^*}}{2N_{3dxy}{}^{\mu^{2p}}}\right]^2 \times 2[S(3d_\delta{}^{\mu_{2p}}, 4d\delta)]^2 \quad (4)$$

B. $^2B_2 \longrightarrow {}^2E(II)$, f = 1.085 ×

$$10^{-5}\,(\nu_{\mathrm{cm.}^{-1}})\left[\frac{N_{2p}c_2{}^{e\pi^b}}{2N_{3dxy}{}^{\mu_{2p}}}\right]^2 \times 2[S(3d_\delta{}^{\mu_{2p}}, 4d\delta)]^2 \quad (5)$$

C. $^2B_2 \longrightarrow {}^2B_2(I), {}^2B_2(II)$, $f = 1.085 \times 10^{-5}(\nu_{\mathrm{cm.}^{-1}}) \times$

$$\left[\frac{2(c_1{}^{e_\pi{}^b}c_2{}^{e_\pi{}^*} + c_1{}^{e_\pi{}^*}c_2{}^{e_\pi{}^b})N_{2p}}{N_{3dxz,yz}{}^{\mu_{2p}}}\right]^2 \times [S(3d_\pi{}^{2p}, 4d_\pi)]^2 \quad (6)$$

D. $^2B_2 \longrightarrow {}^2E(III), {}^2E(IV)$, $f = 1.085 \times 10^{-5}\,(\nu_{\mathrm{cm.}^{-1}}) \times$

$$2\left\{\left[\frac{N_{3p}c_1{}^{e_\pi{}^b}c_2{}^{b_1{}^*}S(4d_\pi{}^{\mu_{3p}}, 4d_\pi)}{N_{4dxz,yz}{}^{\mu_{3p}}}\right]^2 + 2\left[\frac{N_{2p}c_1{}^{b_1{}^*}c_2{}^{e_\pi{}^b}S(3d_\delta{}^{\mu_{2p}}, 4d_\delta)}{2N_{3dxy}{}^{\mu_{2p}}}\right]^2\right\} \quad (7)$$

Notation: N_{np} is a normalization constant for an atomic p orbital; $N_{nd}{}^{\mu_{(n-1)p}}$ is a normalization constant for a nd orbital with a $\mu_{(n-1)p}$ radial exponential factor; $S(nd^{\mu_{(n-1)p}}, 4d)$ is a two-atom overlap integral between a nd ligand orbital with radial exponential factor $\mu_{(n-1)p}$, and a molybdenum 4d orbital; finally, $c_{1\text{ or }2}{}^{\mathrm{M.O.}}$ is an atomic orbital coefficient of eq. 2 for a particular molecular orbital (see Fig. 2).

The predicted f's of Table III are obtained from eq. 4–7 by evaluating the overlap integrals for μ values calculated using Slater's rules, and further assuming $c_1{}^* = c_2{}^b = 0.92$, $c_1{}^b = 0.40$, and $c_2{}^* = -0.40$, in agreement with the coefficients arrived at in the $\mathrm{VO(H_2O)_5}^{2+}$ calculation.[3] The Mo–O distance is taken as 2 Å., and the Mo–Cl distance is taken to be 2.3 Å.

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Binuclear Intermediates in the Reaction between Uranium(VI) and Chromium(II)[1]

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It has been found that at least one binuclear intermediate forms rapidly when Cr(II) and U(VI) are mixed in acid solutions near 0°. The spectrum of the intermediate indicates that it is a substituted Cr(III) species. The intermediate reacts with Tl(III) and V(IV) at rates which are first order in the intermediate concentration but zero order in the concentration of oxidizing agent. In the absence of other reactants the intermediate decomposes to give U(IV), U(VI), and Cr(III) with apparent half-times at 0° ranging between 4 and 8 min. Chemical, optical and kinetic evidence have been found for the presence of significant amounts of a second, more reactive, intermediate in the system.

Introduction

A study of the reaction between U(VI) and Cr(II) in aqueous solution was undertaken to provide further information on the factors which influence the rates of reactions between positive ions. Cr(II) is a particularly interesting reducing agent since the product, Cr(III), is substitution inert.[2]

The kinetics of two other reductions of U(VI) already have been studied: the reaction with Sn(II) in HCl solutions[3] and with Fe(II) in $\mathrm{H_3PO_4}$ solutions.[4] In both of these examples the reactions occur in strongly complexing media. Cr(II), however, is strong enough to reduce U(VI) in perchlorate solutions.

In the present work it has been found that the reaction between U(VI) and Cr(II) is complicated in that the reactants disappear much faster than the final products appear. When the reactants are mixed in acid solutions near 0° a very rapid reaction occurs which gives a bright bottle-green solution. This is followed by a slower reaction to give a darker green solution, characteristic of the final products, U(IV) and Cr(III). This paper gives the details of the evidence for the existence of intermediates in the reaction and also presents some chemistry of the intermediates.

The formation of intermediates in oxidation–

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission and was presented in part at the 138th National A.C.S. Meeting, New York, N. Y., September, 1960.

[2] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[3] R. L. Moore, *ibid.*, **77**, 1504 (1955).

[4] C. F. Baes, Jr., *J. Phys. Chem.*, **60**, 805 (1956).

reduction reactions is not unprecedented. For example, Taube and Myers[2] report that Cr(II) and $Ir(Cl)_6^{-2}$ react rapidly to give an intermediate which decomposes to $Cr(H_2O)_6^{+3}$ and $Ir(Cl)_6^{-3}$ at a lower rate. Also, kinetic evidence has been given for the existence of an intermediate in the reaction between U(IV) and Pu(VI).[5] The intermediate in the Cr(II)–U(VI) reaction resembles the second example in that it is formed between cations in a non-complexing medium.

The intermediates found in the present study probably are similar to the stable complex which recently was found to form between Cr(III) and Np(V).[6]

Experimental Methods

Reagents.—Cr(III) perchlorate was prepared by the dissolution of Mallinckrodt $K_2Cr_2O_7$ in $HClO_4$, filtration of the $KClO_4$ formed, and reduction of the Cr(VI) with analytical grade 30% H_2O_2. Excess H_2O_2 was removed by boiling the solutions. The final $HClO_4$ concentration in the Cr(III) stock solutions was 1 *M*. Most of the Cr(II) perchlorate stock solutions were prepared by the reduction of Cr(III) solutions with amalgamated zinc. That the Zn(II) in these solutions had no effect on the rates was shown by the use of Cr(II) solutions which had been prepared electrolytically using a mercury cathode.

U(VI) perchlorate was prepared by the dissolution of pure U_3O_8 in hot concentrated $HClO_4$. Dilution with water gave a solution which was 0.8 *M* in $HClO_4$. Tl(III) perchlorate solutions were prepared by the dissolution of Tl_2O_3 in a minimum volume of hot $HClO_4$; this solution was cooled to give crystals of thallic perchlorate which were filtered and dissolved in 1.5 *M* $HClO_4$. V(IV) perchlorate was prepared from Fisher Scientific Co. purified $VO(SO_4)_2 \cdot H_2O$. This salt was dissolved in water and precipitated hot with concentrated NH_4OH. The resulting hydroxide was dissolved in $HClO_4$. The precipitation was repeated to remove the last traces of sulfate. The final $HClO_4$ concentration was 0.6 *M*. The solution was analyzed spectrophotometrically by the use of published extinction coefficients.[7] The $HClO_4$ was analytical reagent grade 71% acid.

Fe(III) perchlorate was prepared by the dissolution of analytical grade iron wire in $HClO_4$ followed by oxidation with H_2O_2; the excess H_2O_2 was removed by boiling. The final $HClO_4$ concentration was 1.5 *M*.

Apparatus.—Cr(II) solutions were stored under purified argon in the reservoirs of self-filling burets. All solutions were swept with argon before use. Non-spectrophotometric runs were made in flasks fitted with side tubes for the passage of argon. The solutions were stirred with Teflon covered magnetic stirring bars. Temperatures of 0° were maintained by the use of melting ice. Samples were taken with ice-jacketed pipets, the tips of which had been ground down to deliver in about 7 sec. No provisions were made for excluding light from the room, since essentially the same results were obtained in room light, in a darkened room, and in the very low level monochromatic light in the spectrophotometer.

The spectrophotometric measurements were made with a Cary recording spectrophotometer, Model 14. The thermostated cell holder and the two-chambered mixing cell have been described previously.[5] The cells were flushed with argon before and during filling.

Measurements of *p*H were made with a Beckman Model G meter. The calomel reference electrode was separated from the experimental solutions by a bridge containing 2 *M* $NaNO_3$.

Results

Spectrophotometric Evidence for Intermediates.—U(VI) and Cr(II) were mixed in 1 *M* $HClO_4$ at 2.5° such that the initial concentrations were 2.3×10^{-3} and 1.5×10^{-3} *M*, respectively. After mixing the solutions, their absorbances at several wave lengths were determined as a function of time. The initial rates of change were not high; so precise extrapolation to the time of mixing was possible. At 6438, 6000, 5000, and 4125 Å. the extrapolated absorbance values were 0.155, 0.250, 0.080, and 0.604, while the corresponding values calculated from the sum of the absorptions of the individual reactants were 0.055, 0.034, 0.006, and 0.326, respectively. Thus at all four wave lengths the absorbances extrapolated to time of mixing were significantly higher than those required for no reaction. This is evidence for a rapid reaction followed by a slower one. As the reaction then proceeded to the final products the absorbances at 6438 and 5000 Å. increased while those at 6000 and 4125 Å. decreased. These observations indicate that the intermediates absorb more strongly at these latter wave lengths than either the original reactants or the final products.

In another experiment Cr(II) and U(VI) were mixed in 1 *M* $HClO_4$ at 2.5° such that the initial concentrations of each were 2.3×10^{-3} *M*. The absorbance, *A*, of the solution was determined alternately at 4130 and 6478 Å., where the greatest changes occur. Plots of $\log (A - A_\infty)$ at 4130 Å. and of $\log (A_\infty - A)$ at 6478 Å. *vs.* time both were reasonably straight lines with slopes corresponding to reaction half-times of 4.4 and 5.8 min., respectively. Interpolated values are given in Table I.

The discordant values of the half-times for the disappearance of intermediate are not consistent with any scheme which involves the reaction of a single intermediate to give products. This is shown by the following argument. Consider a

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(5) T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

(6) J. C. Sullivan, private communication.

(7) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).

Table I

Spectrophotometric Run in 1 *M* $HClO_4$ at 2.5°. Cr(II) and U(VI) Each 2.3×10^{-3} *M*

Time, min.	$(A - A_\infty)_{4130}$[a]	$(A_\infty - A)_{6478}$[a]	$(A_\infty - A)_{6478}/(A - A_\infty)_{4130}$
0	0.226	0.439	1.94
2	.169	.387	2.29
4	.122	.305	2.50
6	.091	.240	2.64
8	.067	.190	2.84
10	.049	.150	3.06
12	.036	.118	3.28
14	.027	.093	3.45
16	.019	.074	3.90

[a] Interpolated values.

set of intermediates which may be called X_1, X_2, . . ., X_i, . . . which undergo the net reactions $X_i = m_i\text{Cr(III)} + n_i\text{U(IV)} + p_i\text{U(VI)}$ where the m_i, n_i, and p_i are stoichiometric coefficients, which may be positive, negative, or zero. If Beer's law is assumed it may be shown that for unit path length

$$(A - A_\infty) = [\Sigma(X_i)]\{\Sigma a_i(\epsilon_{X_i} - m_i\epsilon_{\text{Cr(III)}} - n_i\epsilon_{\text{U(IV)}} - p_i\epsilon_{\text{U(VI)}})\} \quad (1)$$

where $a_i = (X_i)/\Sigma(X_i)$, and the ϵ's are the indicated extinction coefficients. This equation should apply at any wave length; dividing two such expressions gives $(A - A_\infty)_1/(A - A_\infty)_2 = B_1/B_2$, where B stands for the quantity given in braces and the subscripts stand for the different wave lengths. Thus if there is only one intermediate the quantity $(A - A_\infty)_1/(A - A_\infty)_2$ should be constant and depend only on the ϵ values irrespective of the equation for, or the mechanism of, the decomposition of X. The results of treating the data in this way are shown in the last column of Table I. The lack of constancy in the absorbance difference ratio shows that the fractions of the various intermediates, the a_i values, are not constant during the decomposition and thus more than one intermediate must be present.

The Rate of Formation of the Intermediates.—An experiment in which Tl(III) and U(VI) were allowed to compete for Cr(II) showed that although the Tl(III)–Cr(II) reaction is very rapid the U(VI)–Cr(II) reaction is of comparable rate since intermediates are formed in the presence of Tl(III). The experimental details were as follows: Tl(III), U(VI), and Cr(II) were mixed in 1 *M* $HClO_4$, such that their initial concentrations were 0.0024, 0.014, and 0.0052 *M*, respectively. The absorbance of the solution was determined as a function of time at 6478 Å. and was found to decrease with a half-time of about 3 min. A preliminary experiment indicated that the reaction in a solution initially 0.024 *M* Tl(III), 0.0052 *M* Cr(II), and 1 *M* $HClO_4$ was 99% complete in less than 20 sec. at 2.5°. Similar experiments have shown that intermediates are formed from Cr(II) and U(VI) in the presence of Fe(III), which also is known to react very rapidly with Cr(II).

Chemical Analysis for the Intermediates.—Tl(III) appeared to be a possible reagent for the intermediates in the U(VI)–Cr(II) reaction since Harkness and Halpern[8] have shown that the U(IV)–Tl(III) reaction is slow. Tl(III) is particularly convenient since its reduction product, Tl(I), does not react with Ce(IV) in $HClO_4$ or H_2SO_4.

An experiment designed to show that Tl(III) reacts quantitatively with the intermediates was as follows. Intermediates were formed by mixing Cr(II) and U(VI) at 0° in 0.1 *M* $HClO_4$ such that their initial concentrations were 0.00643 and 0.0772 *M*, respectively. Periodically, 25-ml. aliquots were removed and added to 100 ml. of 0.00083 *M* Tl(III) in 1 *M* $HClO_4$, also at 0°. These Tl(III) solutions were allowed to stand 35 min. in ice, excess standard ceric perchlorate was added, and the solutions were titrated with standard Fe(II) to determine the amount of reducing agent present. The decomposition of the intermediates produces U(IV) which does not reduce Tl(III); so the reducing agent found increases with time as shown in Table II. Extrapolation to the time of mixing gives a value which is 1% of the Cr(II) added. Thus, at the time of mixing at least 99% of the reducing agent was in a form which can be oxidized by Tl(III) in 35 min. This means that under the conditions used the Tl(III) reacted with at least 99% of the intermediates. The concentration of the intermediates is calculated from the difference between the total reducing agent present and that left after 35 min. with Tl(III) in 1 *M* $HClO_4$ at 0°. Other experiments have shown that the ratio of the intermediates formed to the Cr(II) added depends on the conditions under which the Cr(II) is added to the U(VI). Larger ratios were observed the higher the stirring rate, the higher the U(VI)/Cr(II) ratio, and the lower the acid concentration.

Stoichiometry of the Cr(II)–U(VI) Reaction.—The Tl(III) method of analyzing for intermediates

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[8] A. C. Harkness and J. Halpern, *J. Am. Chem. Soc.*, **81**, 3526 (1959). The rate law was found to be $-d[\text{U(IV)}]/dt = [U^{+4}]\cdot[Tl^{+3}](k_1[H^+]^{-1} + k_2[H^+]^{-2})$. Extrapolation to 0° gives $k_1 = 4 \times 10^{-4}$ sec.$^{-1}$ and $k_2 = 6 \times 10^{-4}$ *M* sec.$^{-1}$.

TABLE II

ANALYSIS FOR INTERMEDIATES

Time sample removed, min.	0[a]	1.8	2.8	4.2	6.8	9.2	15.1	21.3
Reducing agent found, $N \times 10^3$	(0.06)[b]	0.24	0.48	0.95	1.84	2.58	3.99	4.78

[a] Time at which half the Cr(II) had been added. [b] Extrapolated value.

TABLE III

INTERMEDIATE FORMED AS A FUNCTION OF THE INITIAL Cr(II)/U(VI) RATIO

Conditions: 0°; 1 M $HClO_4$; 0.08 M U(VI)

Cr(II)/U(VI)	0.76	0.87	0.99	1.14	1.25	1.33	1.58	1.82	1.99
Int./U(VI)	.66	.70	.79	0.72	0.69	0.65	0.40	0.19	0.07

has been used to determine the stoichiometry of the reaction in which the intermediates are formed. Varying amounts of Cr(II) were added to essentially constant amounts of U(VI) in 1 M $HClO_4$ at 0°. Samples were taken 0.5 min. after mixing and the total intermediate determined. The results of this experiment are shown in Table III. These data show that under similar conditions of mixing, the maximum amount of intermediate is formed when the Cr(II)/U(VI) ratio is close to unity. This requires that one Cr(II) react with one U(VI). At ratios greater than unity, the amount of intermediate decreases, approaching zero as the ratio becomes two. This means that excess Cr(II) reacts with the intermediate to give the final products. Thus larger amounts of intermediate are formed at high stirring rates and low Cr(II)/U(VI) ratios because these conditions minimize local excesses of Cr(II).

Experiments were done in which the pH and intermediate concentrations were determined during the decomposition of the intermediates. The ratio (change in H^+ concentration)/(change in intermediate concentration) was computed for the major portion of the reaction. In four experiments in which the change in H^+ was about 0.025 M the ratios were 2.0, 1.9, 1.8, and 1.9. An uncertainty of 0.01 in pH would make these ratios uncertain by 0.2; so the ratio may be taken as 2 within the experimental error. The over-all reaction for the reduction of U(VI) to U(IV) is $2Cr^{+2} + UO_2^{+2} + 4H^+ = 2Cr^{+3} + U^{+4} + 2H_2O$. This has a H^+/Cr^{+2} ratio of two; so it may be concluded that the formation of the intermediate involves neither a loss nor gain of H^+.

The Reaction between the Intermediates and Tl(III).—This reaction was found to be first order in the concentration of intermediates but zero order in the Tl(III) concentration. The experiments which lead to this conclusion are discussed below.

Cr(II) was added to a U(VI)–Tl(III) mixture at 0° such that the concentrations before reaction were 0.0155, 0.0772, and 0.011 M, respectively; the $HClO_4$ was 1 M. Aliquots of 10 ml. were removed periodically and added to excess Ce(IV). These solutions were titrated with standard Fe(II) to determine total reducing agent, except Tl(I), as a function of time. The results of these titrations are given in Table IV.

TABLE IV

REACTION BETWEEN INTERMEDIATES AND Tl(III) IN 1 M $HClO_4$ AT 0°

t, time of sampling, min.	Reducing agent found, $N \times 10^3$	Intermediate $N \times 10^3$	Calcd.[a] $N \times 10^3$
0	..	..	7.79
0.55	7.76	7.06	7.00
1.4	6.58	5.87	5.93
2.5	5.44	4.73	4.79
3.9	4.23	3.53	3.63
8.1	2.28	1.58	1.60
9.95	1.80	1.10	1.12
12.0	1.45	0.74	0.75
14.0	1.24	0.54	0.51
30.5	0.74	...	...
33.0	.75	...	...
36	.66	...	...
39	.68	...	...
42	.68	...	...

[a] Calculated using: (intermediate) = 0.00779 × $e^{-0.693}/t^{3.55}$.

It is seen that as the intermediates react with Tl(III) to form Tl(I) the concentration of substances oxidized by Ce(IV) ("reducing agent found") decreases. After about 30 min., when the intermediates all have reacted, this concentration becomes essentially constant. This residual reducing agent very probably is U(IV) which was formed during the addition of Cr(II) and it remains constant during the reaction between the intermediates and Tl(III). The possibility that the reaction between intermediates and Tl(III) induces the U(IV)–Tl(III) reaction was investigated and found to be unimportant.

As indicated in the table, a plot of the log of the intermediate concentration *vs.* time gives a good straight line with a half-time of 3.55 min. The average difference between the observed values and those calculated from this line corresponds to a titration difference of 0.013 ml. of the standard Fe(II) solution. The linear log plot requires that the reaction be first order in the concentration of the intermediates and zero order in the Tl(III) concentration. The order in Tl(III) has been confirmed in a series of experiments in which the Tl(III) concentration was varied by a factor of 36 with essentially no change in the apparent half-time for the disappearance of intermediates. In these experiments Cr(II) was added to U(VI) in 1 *M* $HClO_4$ at 0°. Most of this mixture was added to a Tl(III) solution and the reaction was followed as described above. The rest of the mixture was analyzed for total reducing agent. The results of these experiments are given in Table V. In all cases the first order plots were linear for three or four half-times. The data in Table V show that the half-times do not depend on the Tl(III) concentration, nor do they depend on the concentrations of Cr(III), U(VI), or U(IV).

Table V

Reaction between Tl(III) and Intermediates in 1 *M* $HClO_4$ at 0°

Concentrations,[a] $M \times 10^3$					Half-time, min.
Tl(III)	Int.	Cr(III)	U(IV)	U(VI)	
1.0	1.9	0.2	0.1	2.1	3.8
3.3	4.3	0.8	0.4	5.3	3.7
5.0	3.4	2.1	1.0	4.0	3.5
5.0	4.3	0.9	0.4	4.0	3.5
5.5	9.8	2.0	1.0	9.4	3.5
5.5	10.0	2.7	5.5	13.3	3.6
5.5	3.5	22.7	11.3	16.6	3.7
7.5	9.8	4.8	2.4	15.4	3.5
7.5	9.6	4.8	2.4	13.8	3.6
36.5	9.6	4.7	2.4	13.8	3.6

[a] These were the concentrations at the time the solutions were mixed with Tl(III).

For each run the reducing agent concentrations determined during the course of the reaction were extrapolated to the time of mixing and compared with the value calculated from the analysis made on the original Cr(II)–U(VI) mixture. For all the runs in Table V the extrapolated values were in the range of 84 to 93% of the calculated ones. This strongly suggests that some of the intermediates react rapidly with Tl(III) while the rest react with a half-time of about 3.6 min. This is consistent with the spectrophotometric evidence for more than one intermediate referred to earlier.

The amount of rapid reacting intermediate depends on the age and concentration of the U(VI)–Cr(II) mixture which is added to the Tl(III). The effect of age is shown by an experiment made in 1 *M* $HClO_4$ at 0°. Cr(II) and U(VI) were mixed and samples were added to Tl(III) 1 min. and 14 min. after mixing. The 1-min. sample showed 12% rapid reacting intermediate while the 14-min. sample showed 30%. Additional experiments were in agreement with this result.

The effect of concentration is shown by the following experiment. Mixtures initially 0.026 *M* U(VI) and 0.008 *M* Cr(II) in 0.2 *M* $HClO_4$ were added to Tl(III) 2 min. after preparation. Two different runs gave 22.3 and 22.7% rapid reacting intermediate. Companion runs using mixtures initially 0.16 *M* U(VI) and 0.08 *M* Cr(II) in 2 *M* $HClO_4$ gave 9.6 and 10.3% rapid acting intermediate. The volumes were chosen such that the final concentrations in the Tl(III) solutions were all the same.

It was found that small concentrations of H_2SO_4 increase the rate of the Tl(III)–intermediate reaction. In 1 *M* $HClO_4$ at 0° concentrations of H_2SO_4 of 0.013 and 0.050 *M* gave reactions with half-times of 2.8 and 1.9 min., respectively. The initial Tl(III) and U(VI) concentrations were 0.004 and 0.013 *M*, respectively. The amounts of rapid reacting intermediate were found to be 11 and 12%, in agreement with runs without H_2SO_4. The presence of H_2SO_4 did not affect the order with respect to the reactants.

The Spectrum of the 3.6-Minute Intermediate.—The spectrum of that fraction of the intermediate which reacts with Tl(III) with a 3.6-min. half-time at 0° has been determined by a combination of spectrophotometric and titrimetric observations. The equation for the net reaction between Tl(III) and the intermediate may be written

$$\text{Int.} + 1/2\text{Tl(III)} = \text{U(VI)} + \text{Cr(III)} + 1/2\text{Tl(I)} \quad (2)$$

and for unit path length it can be shown that

$$(A - A_\infty) = (\text{Int.})[\epsilon_{\text{Int.}} - \epsilon_{\text{U(VI)}} - \epsilon_{\text{Cr(III)}}] \quad (3)$$

The extinction coefficients for Tl(I) and Tl(III) have been omitted since they are zero in the region of present interest. Equation 3 shows that $(A - A_\infty)$ is proportional to the intermediate concentration and, indeed, in three experiments made at 4100, 4300, and 4500 Å., plots of log $(A - A_\infty)$ were linear with half-times of 3.7, 3.7, and 3.6 min., respectively. At the same time the absorbances were determined the concentrations of intermediate were determined by titration as previously described. This allowed the determination of the extinction coefficient difference given in brackets in (3). Other wave lengths were studied similarly except that the titrations were omitted and the intermediate concentrations were calculated using eq. 3 at one of the wave lengths where the extinction coefficient difference already had been determined. Values of $\epsilon_{\text{Int.}}$ then were calculated by adding the known ϵ values of U(VI) and Cr(III) to the differences. The results of these measurements are summarized in the spectrum shown in Fig. 1. It is seen that this spectrum is quite similar to that of many Cr(III) ions; this suggests that the intermediate examined is a complex formed between Cr(III) and U(V).

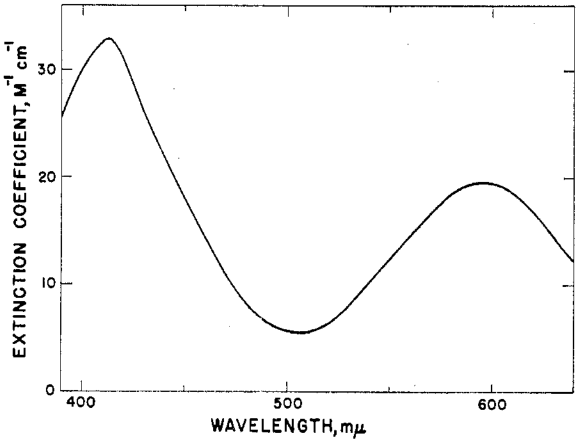

Figure 1.

It was found that the Cr(III) species formed in the reaction represented by eq. 2 is $Cr(H_2O)_6^{+3}$. The spectra of solutions prepared by mixing the same amounts of U(VI), Cr(II), Tl(III), and Fe(III) in different orders were compared. When the order of mixing was Fe(III), Cr(II), Tl(III), U(VI) the spectrum between 3000 and 7000 Å. was found to be essentially the same as when the mixture was made in the first order listed. Since the reaction between Cr(II) and Fe(III) is known[9] to give $Cr(H_2O)_6^{+3}$ it may be concluded that the reaction between intermediates and Tl(III) gives the hexaaquo Cr(III) ion also. When the order was Tl(III), Cr(II), U(VI), Fe(III) the spectrum differed significantly. This is in accord with the observation of Ardon and Plane[9] that the oxidation of Cr(II) by Tl(III) does not give $Cr(H_2O)_6^{+3}$.

Similar experiments showed that when the intermediates decompose in the absence of Tl(III), the Cr(III) product is again the hexaaquo ion.

The Reaction between the Intermediates and V(IV).—The fact that the reaction between Tl(III) and a large fraction of the intermediates is zero order in Tl(III) implies the formation of a more reactive species prior to the reduction of Tl(III). It might be expected, then, that other oxidizing agents should exist which react with the same mechanism and with the same rate. The reaction between V(IV) and intermediates was investigated and found to be zero order in the V(IV) concentration and to have rates nearly one half of the corresponding one for the Tl(III) reaction. This factor of two is understandable since the reduction of Tl(III) to Tl(I) involves two equivalents per mole while V(IV) to V(III) involves only one.

In these experiments Cr(II) was added to U(VI)–V(IV) mixtures using the two-chambered mixing cell. Plots of log $(A - A_\infty)$ were satisfactorily straight and were used for calculating apparent half-times. The results of these experiments are summarized in Table VI.

TABLE VI

REACTION BETWEEN INTERMEDIATES AND V(IV)

Initial concentrations, $M \times 10^3$				Wave length, Å.	Temp., °C.	Half-time, min.
$HClO_4$	U(VI)	V(IV)	Cr(II)			
200	25	9.9	7.5	8000	0.2	6.7
100	25	9.9	7.5	8000	.2	5.7, 6.4, 7.0[a]
500	25	9.9	7.5	8000	.2	7.4
760	25	9.9	7.5	8000	.2	7.05
1000	25	9.9	7.5	8000	.2	7.4
1000	25	15	7.5	8000	.2	7.4
1000	18.6	9.9	9.0	4350	.2	7.6, 7.4
1000	18.6	19.9	9.0	4350	.2	7.3
500	18.6	9.9	9.0	4350	.2	7.4
2000	18.6	9.9	9.0	4350	.2	6.7
1000	23.7	9.5	8.1	8000	10.2	1.9
1000	23.7	9.5	8.1	8000	9.9	1.9
1000	23.7	9.5	8.1	4200	10.0	1.9
1000	23.7	9.5	8.1	4200	10.2	2.0
1000	12.4	9.9	8.1	4200	10.2	2.16
1000	12.4	9.9	8.1	4300	10.2	2.0
1000	12.4	9.9	8.1	4350	10.2	2.0

[a] This last value was obtained using a solution containing $NaClO_4$ to make $\mu = 2$.

The values obtained at 8000 Å. are considered less reliable than the others, since at this wave length the spectrophotometer permits unmonochromatized light to pass through the sample; this causes unavoidable heating in the light path. Variation in $HClO_4$ concentration between 0.10

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

and 2 M has but a small effect, particularly if the ionic strength is held constant.

In order to vary the V(IV) concentration more widely, additional experiments were made in which Cr(II) first was added to U(VI) in 1 M $HClO_4$ at 0° and then the V(IV) was added. This procedure prevents competition between U(VI) and V(IV) for the Cr(II). When the initial concentrations of Cr(II) and U(VI) were 0.0089 and 0.019 M, respectively, changing the V(IV) concentration from 0.0096 to 0.096 M increased the rate an average of only 1.4% and a maximum of 4.3%.

The data of Table VI were used to calculate values for the activation energy and entropy of activation for the first order reaction in which the principal intermediate is converted to the reactive one. The values 20 kcal./mole and +0.5 e.u. were obtained.

The Reaction between the Intermediates and Other Reagents.—No slowness has been observed in the reaction between the intermediates and either Ce(IV) or Cr(VI).

The effect of dissolved oxygen was determined in experiments in 2 M $HClO_4$ at 0°. Under these conditions the rate of the reaction between U(IV) and oxygen is negligibly slow.[10] Cr(II) and U(VI) were mixed and added to a large volume of rapidly stirred, oxygen-saturated $HClO_4$ such that the concentrations just after mixing were 5.9×10^{-3} M Cr(III), 3.1×10^{-3} M U(VI), 0.9×10^{-3} M U(IV), and 4.0×10^{-3} N total intermediate. The oxygen concentration was estimated to be 4.6×10^{-3} N. Samples of this mixture were analyzed for total reducing agent (intermediates + U(IV)) and reducing agent not oxidized by Tl(III) (only U(IV)) as a function of time. It was found that the total reducing agent concentration decreased because of the oxygen reaction, but at the same time the U(IV) concentration increased. The concentration of intermediates was calculated, as described above, from the difference between the two directly measured quantities; the rate of its disappearance was found to be the same as in similar solutions through which argon was passed. This implies that oxygen is like Tl(III) in that it does not react directly with the predominant intermediate. The rates of decrease in total intermediate concentration were compared with the decrease in the total reducing agent concentration. The ratio d[total reducing agent]/d[intermediate] went from about $^1/_3$ near the start of the reaction up to about 1.2 near the end. Thus when the intermediate concentration was high about $^3/_4$ of it decomposed to give U(IV), while near the end of the reaction it essentially all reacted with oxygen.

Fe(III) reacts at a measurable rate with the intermediates, but unlike Tl(III) and V(IV) the rate is not zero order in the oxidizing agent. Experiments were done at 0° in solutions approximately 0.2 M in $HClO_4$. This concentration of acid was used in order to minimize interference by the U(IV)–Fe(III) reaction. U(VI) and Cr(II) were mixed and then Fe(III) was added such that the initial concentrations were 0.019, 0.0089, and 0.010 M, respectively. The absorbance of the mixture was determined as a function of time at 4500 Å. at 0.2°. A plot of log $(A - A_\infty)$ showed curvature; the initial slope corresponded to a half-time of 3 min. Repeat experiments in which the Fe(III) concentrations were 0.020 and 0.028 M in Fe(III) and 0.20 and 0.22 M in $HClO_4$ gave initial half-times of 1.5 and 0.9 min., respectively. These results show that the reaction is not zero order but probably mixed zero and first order in Fe(III).

A qualitative determination of the rate of the reaction between U(V) and the intermediates showed that this rate is quite low. U(V), prepared by the reduction of U(VI) with Eu(II), was added to a mixture of U(VI) and Cr(II). The initial concentrations were estimated to be 0.0022 M U(V), 0.0029 M total intermediates, and 0.5 M $HClO_4$. From the rate of formation of U(IV) (determined by the Tl(III) method) it was concluded that the rate of disappearance of U(V) was no greater than that to be expected by disproportionation. The disproportionation rate was estimated by extrapolating the data of Imai[11] for ionic strength 2 to 0°.

Intermediates in Other Cr(II) Reactions.—In experiments in which Cr(II) was added to U(VI)–V(IV) mixtures an initial rapid decrease in absorption was observed. Since this could be explained by assuming that an intermediate is formed in the Cr(II)–V(IV) reaction, this possibility was investigated further. In the reaction V(IV) + Cr(II) = V(III) + Cr(III) the absorption at 4300 Å. should increase since the appropriate ϵ values are about 0, 0.9, 1, and 12 M^{-1} cm.$^{-1}$, respectively. However, when Cr(II) and V(IV) were mixed in 1 M $HClO_4$ at 0.2° the ab-

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[10] J. Halpern and J. G. Smith, *Can. J. Chem.*, **34**, 1419 (1956).

[11] H. Imai, *Bull. Chem. Soc. Japan*, **30**, 873 (1957).

sorbance was found to decrease, approaching its final value with a half-time of about 0.25 min. This observation can be explained by the rapid formation of an intermediate which then decomposes. Four experiments in which the Cr(II) concentration ranged between 0.007 and 0.01 *M* and the V(IV) concentration ranged between 0.02 and 0.083 *M* gave apparent half-times ranging between 0.28 and 0.26 min.

Experiments in which V(V) and Cr(II) were mixed showed decreases in the absorption rather than the increase which is predicted on the basis of the extinction coefficients. Again, this is evidence for an intermediate. In this case plots of log $(A - A_\infty)$ were not linear; so the decomposition of the intermediate is more complicated than in the Cr(II)–V(IV) reaction.

Due to the similarity between PuO_2^{+2} and UO_2^{+2} experiments were done to see whether an intermediate is formed in the Cr(II)–Pu(VI) reaction. Pu(VI) and Cr(II) were mixed in 1 *M* $HClO_4$ at 0° such that their initial concentrations were 0.012 and 0.0079 *M*, respectively. No evidence for an intermediate was found; the absorbance at 4300 Å. became constant within 15 sec. after mixing.

The Rate of Decomposition of the Intermediates.—The decomposition of the intermediates in the absence of other oxidizing or reducing agents was found to be quite complicated, due in part to the presence of a significant quantity of a relatively reactive intermediate as well as the principal one.

A series of rate runs was made at 0° in perchlorate solutions with an ionic strength of two. The concentrations of total reducing agent and reducing agent left after reaction with Tl(III) were determined as before. It was found that under some conditions small changes in the total reducing agent occurred. This is illustrated by the data in Table VII.

The data show that (1) the higher the initial Cr(II) concentration the smaller the loss, (2) the higher the acid concentration at constant perchlorate concentration the smaller the loss, (3) the higher the perchlorate at constant acid concentration the larger the loss, and (4) the loss is very small at room temperature. These results indicate that one of the reactive intermediates probably reacts with the perchlorate ion.

In following the decomposition, the intermediate concentration was calculated from the difference between the total reducing agent concentration (obtained by interpolation where necessary) and the reducing agent left after reaction with Tl(III). The log of the intermediate concentration was plotted *vs.* time and apparent half-times were determined from the slopes at various concentration values. The results of experiments in 0.2 and 2 *M* $HClO_4$ are given in Tables VIII and IX. It is seen that for runs with low initial concentrations of intermediate the initial half-times are abnormally large but that, in general, the half-times increase as the reaction proceeds. At any particular intermediate concentration the half-times are in reasonable agreement in spite of the varying initial conditions. It is seen that large changes in the concentrations of the reaction products, U(IV), U(VI), and Cr(III), have only small effects on the rates. The effect of acid concentration is small, particularly at the larger intermediate concentrations.

TABLE VII

PER CENT. LOSS OF TOTAL REDUCING AGENT IN 25 MIN. AT 0°

H^+, *M*	U(VI), *M*	ClO_4^-, *M*	Cr(II) added, *M*	% Loss
2.1	0.10	2.1	0.03	0.2
2.0	.008	2	.0026	4
1.0	.010	0.04[a]	.0024	1.7
1.0	.010	...[b]	.0024	0.6
0.2	.029	2.0	.025	< .4
.2	.025	2.0	.019	.8
.2	.035	2.0	.012	1.6
.2	.023	2.0	.0089	2.3
.2	.014	2.0	.0045	7.2
.2	.0075	2.0	.0023	8.4
.2	.080	0.2	.0024	7.7
.21	.010	.21	.003	7.8
.21	.010	.21	.0029	<0.2[c]

[a] HCl added. [b] Saturated with $KClO_4$. [c] Run at room temperature.

Discussion and Interpretation

The data in this paper show that when Cr(II) and U(VI) are mixed in acid solution near 0°, a very rapid reaction occurs which results in at least one intermediate

$$\mathrm{Cr(II)} + \mathrm{U(VI)} = \mathrm{Cr^{III}\cdot U^{V}} \qquad (4)$$

It is probable that the intermediate is a U(V)–Cr(III) species rather than a U(VI)–Cr(II) species since its spectrum is similar to that of other Cr(III) ions. The *p*H experiments indicated that there was no H^+ change in the reaction; so the $[Cr^{III}\cdot U^{V}]$ species is probably $CrOUO^{+4}$. Concurrently with (4) a rapid reaction between $[Cr^{III}\cdot U^{V}]$ and Cr(II) occurs

$$[\mathrm{Cr^{III}\cdot U^{V}}] + \mathrm{Cr(II)} = 2\mathrm{C}\ \mathrm{(III)} + \mathrm{U(IV)} \qquad (5)$$

TABLE VIII

DECOMPOSITION OF INTERMEDIATES (0.2 M $HClO_4$, 1.8 M $NaClO_4$, 0°)

	Initial concentration, $M \times 10^3$				Initial	Apparent half-times, min., at the listed intermediate concentrations, $M \times 10^3$								
	X	U(VI)	Cr(III)	U(IV)	$t_{1/2}$, min.	0.45	0.6	1.0	2.0	4.0	6.0	10	15	20
1	1.9	16	0.0	0.0	15	11.2	8.1	6.9						
2	2.1	5	.0	.0	9.9	8.3	7.7	6.9						
3	4.2	10	.3	.2	7.6	8.9	7.9	7.0	6.2					
4	8.6	14	.3	.2	8.3			7.4	5.9	5.1	5.1			
5	12	23	.1	.1	5.2				6.5	5.4	4.9			
6	17	7	2.1	1.0	4.4				6.3	5.4	5.0	4.6	4.2	
7	20	6	5.0	2.5	3.8				6.6	5.6	5.0	4.4	4.0	3.8
8	21	22	32.0	2.4	4.1					5.9	5.2	4.6	4.3	4.1
9	23	22	2.1	1.0	4.2					5.7	5.1	4.6	4.3	4.2
10	24	77	25.3	12.6	4.6					6.5	5.8	5.0	4.8	4.6
11	25	89	0.4	0.2	5.3					6.3	5.5	4.9	4.5	
Calculated from the derived expression						8.1	7.8	7.2	6.3	5.4	4.9	4.5	4.3	4.15

$t_{1/2} = 7.4[1 + 0.24 + 280(X)][1 + 2 \times 280(X)]^{-1}$

(X) is the concentration of the intermediates.

TABLE IX

DECOMPOSITION OF THE INTERMEDIATES (2 M $HClO_4$, 0°)

	Initial concentration, $M \times 10^3$				Initial	Apparent half-times, min., at the listed intermediate concentrations, $M \times 10^3$									
No.	X	U(VI)	Cr(III)	U(IV)	$t_{1/2}$, min.	0.4	0.6	1.0	2.0	3.0	4.0	6.0	10.0	14.0	20.0
12	1.9	5	0.6	0.3	6.8	6.7	6.3	6.1							
13	2.1	16	.0	.0	9	7.6	6.7	6.1							
14	2.1	5	.1	.1	6.4	7.1	6.5	6.1							
15	3.7	7	.1	.1	5.2	7.7	7.1	6.2	5.5	5.3					
16	5.1	13	1.7	.9	5.5		7.1	6.3	5.8	5.6	5.4				
17	6.4	12	0.4	.2	5.3			6.7	5.9	5.7	5.6	5.3			
18	10.7	8	3.2	1.6	4.6				6.3	5.7	5.3	5.0	4.6		
19	13	20	16	8	4.3				6.6	5.9	5.5	5.0	4.6		
20	20	11	7	26	4.2					6.3	5.9	5.3	4.8	4.5	
21	24	9	3.6	1.8	4.1					6.2	5.8	5.2	4.6	4.4	4.2
22	27	88	0.7	0.4	4.1				6.0	5.5	5.2	4.8	4.6	4.4	4.2
Calculated from the derived expression						7.0	6.8	6.5	6.0	5.6	5.4	5.0	4.6	4.4	4.2

$t_{1/2} = 7.4[1 + 150(X)][1 + 2 \times 150(X)]^{-1}$

(X) is the concentration of the intermediates.

This reaction is consistent with the fact that the amount of intermediate found decreases when the initial Cr(II):U(VI) ratio exceeds unity.

The reaction between the intermediates and V(IV) is first order and zero order in their respective concentrations. This implies that the predominant intermediate reacts to give some species which is capable of rapid reaction with V(IV). The composition of this species is unknown and will be designated by Cr·U* even though it is not certain that the Cr and U are combined.[12]

$$[Cr^{III}\cdot U^{V}] = Cr\cdot U^{*} \qquad (6)$$

$$Cr\cdot U^{*} + V(IV) = Cr(III) + U(VI) + V(III) \qquad (7)$$

Tl(III) also reacts with the intermediates at a rate which is first order in the intermediate but zero order in the Tl(III) concentration; however, the first order rate constant is twice as great as the corresponding one for the V(IV) reaction. This implies that reaction 7 is replaced by two reactions such as

$$Cr\cdot U^{*} + Tl(III) = Cr(III) + U(VI) + Tl(II) \qquad (8)$$

$$Tl(II) + [Cr^{III}\cdot U^{V}] = Cr(III) + U(VI) + Tl(I) \qquad (9)$$

The possibility that the Tl(II) indicated in (8) and (9) actually is combined with U(VI) and/or Cr(III) cannot be excluded. It was shown, however, that the final Cr(III) is the hexaaquo ion.

Although reactions 6, 7, and 8 can be explained just as well by assuming Cr(III) plus ordinary U(V) instead of Cr·U*, this simpler assumption is not consistent with the observations on the decomposition of the intermediates in the absence of other oxidizing agents. The data in Tables VIII and IX show that at relatively high inter-

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(12) The two forms of the intermediate might differ in degree of hydration and bridging, for example $[(H_2O)_5CrOUO]^{+4}$ and $[(H_2O)_4Cr(OH)_2U(OH)_2]^{+4}$. The latter of the forms was suggested by Prof. H. Taube.

mediate concentrations the initial half-times are nearly half that of reaction 6 under comparable conditions. This means that the reactive intermediate, $\mathrm{Cr \cdot U^*}$, reacts rapidly with the predominant one at those concentrations

$$\mathrm{Cr \cdot U^*} + [\mathrm{Cr^{III} \cdot U^V}] = \mathrm{U(IV)} + \mathrm{U(VI)} + 2\mathrm{Cr(III)} \quad (10)$$

Since ordinary U(V) has been shown to react slowly with the intermediates it cannot be the reactive one.

At lower intermediate concentrations the apparent half-times are larger, even exceeding that of (6) in the most dilute solutions. To account for this we postulate the additional reactions

$$\mathrm{Cr \cdot U^*} = \mathrm{Cr(III)} + \mathrm{U(V)} \quad (11)$$

$$\mathrm{Cr \cdot U^*} = \mathrm{Cr^{III} \cdot U^V} \quad (-6)$$

Reaction 11 probably is followed by

$$\mathrm{U(V)} + \mathrm{Cr \cdot U^*} = \mathrm{Cr(III)} + \mathrm{U(IV)} + \mathrm{U(VI)} \quad (12)$$

and/or

$$2\mathrm{U(V)} = \mathrm{U(IV)} + \mathrm{U(VI)} \quad (13)$$

The proposed mechanism for the decomposition of the intermediates consists of the four rate determining reactions 6, −6, 10, and 11. This mechanism is difficult to test against the experimental data since the simultaneous non-linear differential equations which result from it cannot be solved directly without the use of simplifying assumptions. The usual steady-state approximation that $d[\mathrm{Cr \cdot U^*}]/dt = 0$ is suspect since the amount of $\mathrm{Cr \cdot U^*}$, the reactive intermediate, has been shown to be rather large (possibly as much as 15% of the initial total intermediate concentration).

Calculations using the Electronic Associates Inc. analog computer Model 231 R were made in order to gain a qualitative understanding of the kinetics of the proposed mechanism in the non-steady state region. Particular solutions for the differential equations were determined for a number of widely varying values of the rate constants.[13] It was found that in early stages of reaction when the concentration of reactive intermediate goes from zero to its maximum value, the apparent first order rate constant (based on the total intermediate concentration) also rises to a maximum. For the rest of the reaction, the apparent first order rate constant falls off, paralleling that predicted by the usual steady-state approximation.

In an example with behavior similar to that indicated by the experimental data, the apparent first order rate constant rose during the first 40% of the reaction to a value which was about 14% lower than that predicted by the steady-state approximation using the same rate constants. At this point the concentration of the reactive intermediate amounted to about 11% of the initial total intermediate concentration ($\mathrm{Cr^{III} \cdot U^V} + \mathrm{Cr \cdot U^*}$). For the remaining 60% of the reaction the apparent first order rate constant decreased, remaining a little smaller than the steady-state approximate values. Thus it is to be expected that equations having the same form as the steady-state approximate ones will describe the general behavior of the system after the maximum values of the $\mathrm{Cr \cdot U^*}$ concentration have been reached.

The steady state approximation leads to the expression

$$(t_{1/2})' = (t_{1/2})_6 \frac{1 + (k_{-6}/k_{11}) + (k_{10}/k_{11})(\mathrm{Cr^{III} \cdot U^V})}{1 + 2(k_{10}/k_{11})(\mathrm{Cr^{III} \cdot U^V})} \quad (14)$$

where $(t_{1/2})'$ is the apparent half-time, $(t_{1/2})_6$ is the half-time corresponding to reaction 6, the k's are the rate constants of the corresponding reactions, and ($\mathrm{Cr^{III} \cdot U^V}$) is the concentration of the principal intermediate. Equations of the same form as (14) were used to obtain the calculated values given in Tables VIII and IX. Since ($\mathrm{Cr^{III} \cdot U^V}$) was approximated by the total intermediate concentration, the parameters used to reproduce the data cannot be taken as values of the rate constant ratios in (14). It may be concluded, however, that the experimental data are not inconsistent with the proposed mechanism.

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