tence of MnO_3^+ in concentrated solutions of sulfuric acid had been speculated on by Thorpe and Hambly.[11] It is assumed in this mechanism that all protolytic steps are rapid.

That Mn(III) does not participate in any reversible step is shown by its zero-order kinetic dependency, Table III. Reaction 2 may be written as the sum of two rapid steps, the first being an equilibrium step

$$4H^+ + MnO_2 \overset{K_5}{\rightleftarrows} Mn^{4+} + 2H_2O \tag{5}$$

and

$$Mn^{4+} + Mn^{2+} \xrightarrow{k_6} 2Mn^{3+} \tag{6}$$

where $k_2 = K_5k_6$. Reaction 6 has been shown by Bradley and Van Preagh[12] to be rapid and reversible. At our experimental conditions, the product Mn^{3+} is highly favored. This is due to our higher acid concentrations, higher manganous ion concentrations, and the complexation of Mn(III) by SO_4^{2-} ion. This proposed mechanism is in agreement with the observations that there is no induction period and that the observed rate of disappearance of MnO_4^- is equal to the rate of appearance of the product, manganic ion.

Summary

At experimental conditions where Mn(III) is formed as the product rather than MnO_2, the rate expression for the reduction of MnO_4^- by Mn(II) is

$$-\frac{d[MnO_4^-]}{dt} = {}^1/_5\frac{d[Mn(III)]}{dt} =$$

$$\{k_0 + k_1[H^+] + k_2[H^+]^2\}[MnO_4^-][Mn(II)]^2$$

Due to the higher acidity, the higher manganous ion concentrations, and the ability of SO_4^{2-} to complex with manganic ion, the reaction path (mechanism) is necessarily different when Mn(III) rather than MnO_2 is the favored product. Undoubtedly, the electron-exchange reaction between MnO^{2+} and MnO^+ is no longer rate determining as observed by Adamson[5] in perchlorate media. In a few runs made in perchlorate media rather than sulfate media MnO_2 was observed to slowly precipitate out of solution thereby emphasizing the importance of complexation of Mn(III) by SO_4^{2-} to stabilize Mn(III) as the reaction product.

Acknowledgment. The authors acknowledge the National Science Foundation Undergraduate Research Participation Program for partial support of this research.

Registry No. Mn^{2+}, 16397-91-4; MnO_4^-, 14333-13-2.

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[11] T. E. Thorpe and F. J. Hambly, *J. Chem. Soc.*, 13, 175, (1888).

[12] J. Bradley and G. Van Preagh, *J. Chem. Soc.*, 1624 (1938).

Contribution from the Chemical Technology Division,
Australian Atomic Energy Commission, Sydney 2232, Australia

Kinetics and Mechanism of the Decomposition of the Uranium(V)-Chromium(III) Complex and of its Reaction with Excess Chromium(II)

A. EKSTROM

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The kinetics of the decomposition of the $U^V \cdot Cr^{III}$ binuclear complex and of its reaction with excess Cr(II) have been studied. The decomposition of the complex was found to be a first-order process under the experimental conditions used, the values of ΔH^* and ΔS^* being 12.8 ± 0.1 kcal mol^{-1} and −21.2 ± 0.4 eu, respectively. The rate was found to be virtually independent of acid concentration and ionic strength. The rate of reaction between $U^V \cdot Cr^{III}$ and excess Cr(II) was also found to be independent of acid concentration but was strongly influenced by ionic strength, this effect being found consistent with the Debye-Huckel equation. For this reaction $\Delta H^* = 3.16 \pm 0.30$ kcal mol^{-1} and $\Delta S^* = -35.2 \pm 1.0$ eu. Reaction mechanisms consistent with the results are discussed.

Introduction

Excess Cr(II) will reduce U(VI) to U(IV) according to the equation

$$U(VI) + 2Cr(II) + 4H^+ \rightarrow U(IV) + 2Cr(III) + 2H_2O \tag{1}$$

However, as shown previously,[1,2] the mechanism of this reaction is rather complex, the first step being the formation of a U^V-Cr^{III} binuclear complex (reaction 2).

$$U(VI) + Cr(II) \rightarrow U^V \cdot Cr^{III} \tag{2}$$

The kinetics of the formation of the $U^V \cdot Cr^{III}$ complex have recently been examined,[3] and in this paper we describe the results obtained from a study of the kinetics of (a) the decomposition of the intermediate and (b) the reaction of the intermediate with excess Cr(II) according to reaction 3.

$$Cr(II) + U^V \cdot Cr^{III} + 4H^+ \rightarrow U(IV) + 2Cr(III) + 2H_2O \tag{3}$$

The work was undertaken to provide the data necessary for comparing the mechanism and kinetics of the reactions of the $U^V \cdot Cr^{III}$ species with those of analogous systems which have been studied previously.

Experimental Section

Reagents. The procedures used for the preparation of $UO_2(ClO_4)_2$, $NaClO_4$, $HClO_4$, and $DClO_4$ stock solutions and for the preparation and handling of the Cr(II) solutions are described elsewhere.[3]

Measurement of Reaction Rates. An Aminco-Morrow stopped-flow apparatus[3] was used to follow the reactions, but for this work the output of the instrument was recorded by an on-line PDP-8L computer rather than by the more usual storage oscilloscope. In this arrangement (Figure 1), the output of photomultiplier is passed, *via* an amplifier and analog-digital converter, to the core of the computer for storage. The computer is activated *via* the strobe circuit by the closing of the trigger on the stopped-flow apparatus. The system then samples the photomultiplier output at preset time intervals, stores data until the completion of a run, and displays the results *via* a teletype or punched tape. The output consists of a series of numbers

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[1] T. W. Newton and F. B. Baker, *Inorg. Chem.*, 1, 368 (1962).

[2] G. Gordon, *Inorg. Chem.*, 2, 1277 (1963).

[3] A. Ekstrom and Y. Farrar, *Inorg. Chem.*, 11, 2610 (1972).

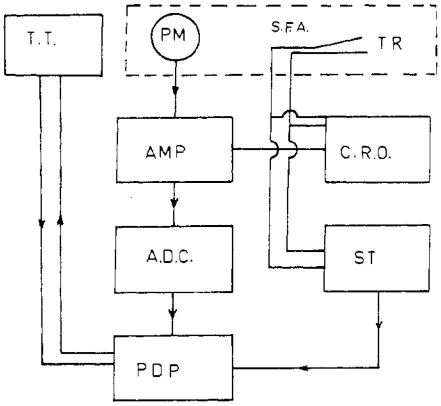

Figure 1. Block diagram of the equipment used for the recording of stopped-flow data with an on-line computer: PM, photomultiplier; TR, trigger; AMP, amplifier; ADC, analog to digital converter; PDP, computer; ST, strobe circuit; CRO, cathode ray oscilloscope; TT, teletype; SFA, stopped-flow apparatus.

whose magnitude is directly proportional to the transmittance of the solution at any time. At present, up to 128 "samples" of the transmittance at any time interval between 1 and 2000 msec can be chosen, although the number of "samples" could be easily increased. The present equipment thus essentially eliminates the tedious and inaccurate reading of oscilloscope pictures, and excellent agreement is obtained for rate curves measured by the conventional method using an oscilloscope and by the method described above.[4]

Calculations. Preliminary experiments showed that the rate of decomposition of the $U^V \cdot Cr^{III}$ complex was given by the rate law

$$-d[U^V \cdot Cr^{III}]/dt = k_4[U^V \cdot Cr^{III}] \tag{4}$$

and hence the value of the rate constant was evaluated from the integrated rate equation

$$\ln (B_0/x) = k_4 t \tag{5}$$

where x is the concentration of the intermediate at any time t and B_0 the concentration of $U^V \cdot Cr^{III}$ at time $t = 0$. Since under conditions where the initial U(VI) concentration is greater than the initial Cr(II) concentration the formation of the intermediate $U^V \cdot Cr^{III}$ is quantitative,[1,3] the value of B_0 is taken as equal to $[Cr(II)]_0$. From the stoichiometry of eq 6 it can be readily shown that the concentration

$$2U^V \cdot Cr^{III} \rightarrow U(VI) + U(IV) + 2Cr(III) \tag{6}$$

(x) of the intermediate at any time is given by the expression

$$x = [2(ABST) - 2\epsilon_{U(VI)}A_0 - B_0(2\epsilon_{Cr(III)} + \epsilon_{U(IV)} - \epsilon_{U(VI)})][2\epsilon_{int} - \epsilon_{U(VI)} - \epsilon_{U(IV)} - 2\epsilon_{Cr(III)}]^{-1} \tag{7}$$

where ABST is the absorbance of the reactant solution at any time and $\epsilon_{Cr(III)}$, $\epsilon_{U(IV)}$, $\epsilon_{U(VI)}$, and ϵ_{int} are the extinction coefficients of Cr(III), U(IV), U(VI), and the $U^V \cdot Cr^{III}$ intermediate, respectively. As the reaction was followed either at 400 or 640 nm, eq 7 can be simplified to the extent that at 400 nm $\epsilon_{U(IV)} = 0$, while at 640 nm $\epsilon_{U(IV)} = 0$. The values of $\epsilon_{Cr(III)}$, $\epsilon_{U(IV)}$, and $\epsilon_{U(VI)}$ were measured independently at each wavelength and condition of acidity, temperature, and ionic strength, while the values of ϵ_{int} were measured as described previously.[3]

The reduction of U(VI) by excess Cr(II) may be described by

$$U(VI) + Cr(II) \xrightarrow{k_8} U^V \cdot Cr^{III} \tag{8}$$

$$U^V \cdot Cr^{III} + Cr(II) \xrightarrow{k_9} U(IV) + 2Cr(III) \tag{9}$$

This reaction sequence can be described by the two simultaneous equations

$$dx/dt = k_8(A_0 - x - y)(B_0 - x - 2y) - k_9 y(B_0 - x - 2y) \tag{10}$$

$$dy/dt = k_9 y(B_0 - x - 2y) \tag{11}$$

where $A_0 = [U(VI)]_0$ and $B_0 = [Cr(II)]_0$ and x and y are the concentrations of $U^V \cdot Cr^{III}$ and U(IV) at any time, respectively. The reaction was followed at 640 nm and the data were analyzed using the Runge-Kutta numerical integration method[5] for eq 10 and 11, in combination with eq 12, and the BMDX[6] nonlinear least-squares program to

$$ABST = x\epsilon_{int} + \epsilon_{Cr(II)}(B_0 - x - 2y) + y(2\epsilon_{Cr(III)} + \epsilon_{U(IV)}) \tag{12}$$

determine the values of k_8 and k_9 which best reproduce the absorbance (ABST) of the reactant solution at any time. The BMDX program requires the partial differentials of eq 12 with respect to the two unknowns (k_8 and k_9) and the values of these differentials were determined using the numerical method described by Bickley.[7] From the stoichiometry of eq 1 it can be readily shown that

$$2\epsilon_{Cr(III)} + \epsilon_{U(IV)} = [ABSF - \epsilon_{Cr(II)}(B_0 - 2A_0)]A_0^{-1} \tag{13}$$

where ABSF is the absorbance of the reactant solution at the completion of the reaction. The value of $2\epsilon_{Cr(III)} + \epsilon_{U(IV)}$ derived from eq 13 and the value of ϵ_{int} measured in the course of the study of the decomposition of the intermediate were used for the evaluation of eq 12.

The value of $\epsilon_{Cr(II)}$ (the extinction coefficient of Cr(II)) was measured independently for each condition of acidity, temperature, and ionic strength. Other calculations requiring nonlinear least-squares analysis were carried out using a program previously described by Lietzke.[8]

Results

(a) Decomposition of the $U^V \cdot Cr^{III}$ Complex. Preliminary experiments on the kinetics of the decomposition of the $U^V \cdot Cr^{III}$ complex had suggested that the reaction obeyed first-order kinetics under the experimental conditions used in this study. This result is confirmed by the observation that the first-order rate constant is independent of the initial U(VI) and Cr(II) concentrations, as well as being independent of the wavelength of the light used to follow the reaction (Table I and Figure 2). The results also show that the values of the extinction coefficient of the intermediate (ϵ_{int}) at 400 and 640 nm are in good agreement with those measured in the previous studies.[1,3]

The rate constant for the decomposition of the intermediate shows only a slight increase with increasing acid concentration, being $(8.47 \pm 0.20) \times 10^{-2}$ sec^{-1} at 0.46 M H$^+$ and $(9.82 \pm 0.09) \times 10^{-2}$ sec^{-1} at 1.98 M H$^+$. The acid dependency is probably due to a medium effect and can be adequately described by a Harned function of the type

$$k = k_0 \exp\{b[H^+]\} \tag{14}$$

with $k_0 = (8.30 \pm 0.12) \times 10^{-2}$ sec^{-1} and $b = 0.087 \pm 0.009$.

Similarly, for a solution 0.374 M in H$^+$, the first-order rate constant was found to be nearly independent of the ionic strength (adjusted with $NaClO_4$). Thus at $I = 1.01$, $k_4 = (8.06 \pm 0.12) \times 10^{-2}$ sec^{-1} and at $I = 4.41$, $k_4 = (10.21 \pm 0.20) \times 10^{-2}$ sec^{-1}. This effect is consistent with the extended Debye-Huckel equation

$$\log k = \log k_0 + [A\Delta Z^2 I^{1/2}/(1 + BaI^{1/2})] + CI \tag{15}$$

since the ΔZ^2 term is zero in this case. Least-squares analysis of the data in terms of eq 15 yielded values of $(7.56 \pm 0.11) \times 10^{-2}$ sec^{-1} and $(2.01 \pm 0.24) \times 10^{-2}$ in the terms k_0 and C, respectively.

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(4) We wish to express our gratitude to Mr. P. Ellis of the Instrument and Control Division (AAEC) for designing and building the data acquisition system. We also wish to thank Mr. I. Liepa for programming of the PDP-8L computer.

(5) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, Van Nostrand, Princeton, N. J., 1956, p 489.

(6) J. M. Barry and P. C. Herald, unpublished work.

(7) W. G. Bickley, *Math. Gaz.*, 25, 19 (1941).

(8) M. H. Lietzke, Report ORNL 3259, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

Table I. Effect of Initial U(VI) and Cr(II) Concentrations on the Rate Constant for the Decomposition of the $U^V \cdot Cr^{III}$ Complex[a]

		640 nm		400 nm	
$10^2[U(VI)]_0$, M	$10^2[Cr(II)]_0$, M	ϵ_{int},[b] M^{-1} cm^{-1}	10^2k_4, sec^{-1}	ϵ_{int},[b] M^{-1} cm^{-1}	10^2k_4, sec^{-1}
7.29	5.63	12.3 ± 0.5	10.11 ± 0.10	29.1 ± 0.9	9.70 ± 0.20
7.29	4.50		10.11 ± 0.10		9.94 ± 0.10
7.29	3.32		10.15 ± 0.15		10.20 ± 0.23
7.29	2.25		9.83 ± 0.20		9.55 ± 0.15
7.29	1.12		9.95 ± 0.30		9.88 ± 0.10
2.43	2.25		9.20 ± 0.20		9.80 ± 0.28
4.86	2.25		8.91 ± 0.15		9.50 ± 0.31
7.29	2.25		9.00 ± 0.17		9.30 ± 0.41
9.73	2.25		8.95 ± 0.26		9.25 ± 0.16
12.1	2.25		9.65 ± 0.32		
14.6	2.25		8.12 ± 0.10		

[a] Conditions: $[H^+]_0 = 2.00\,M$, 30°, ionic strength 3.00. [b] Extinction coefficient of the intermediate.

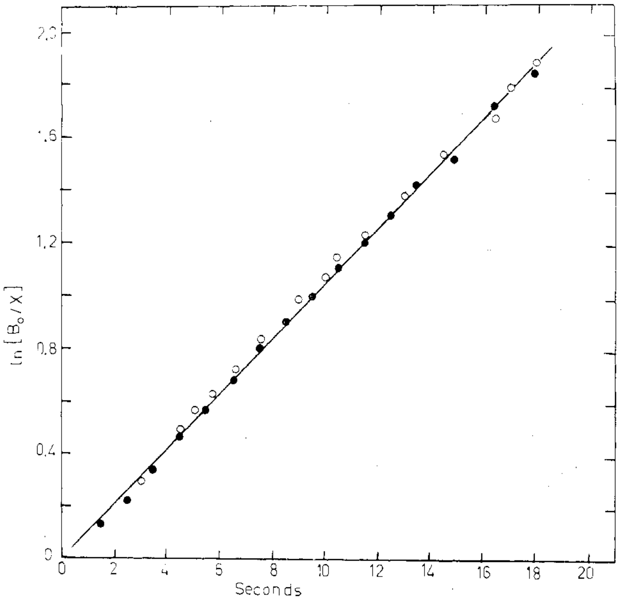

Figure 2. Plot of the integrated rate equation (eq 5) for the decomposition of the $U^V \cdot Cr^{III}$ complex, where $[U(VI)]_0 = 7.29 \times 10^{-2}\,M$, $[Cr(II)]_0 = 4.50 \times 10^{-2}\,M$, $[H^+]_0 = 2.00\,M$, ionic strength is 3.00, and temperature is 30°: ●, reaction measured at 400 nm; ○, reaction measured at 640 nm.

Table II. Temperature Dependency of the Rate Constant for the Decomposition of the $U^V \cdot Cr^{III}$ Complex[a]

Temp, °C	No. of determinations	10^2k_4(obsd), sec^{-1}	10^2k_4(calcd),[b] sec^{-1}
14.0	3	2.33 ± 0.08	2.66
16.0	3	3.30 ± 0.08	3.12
18.0	3	4.16 ± 0.10	3.66
22.5	4	5.35 ± 0.08	5.27
25.5	3	7.14 ± 0.40	6.53
28.5	3	8.43 ± 0.20	8.17
32.0	3	9.72 ± 0.10	10.6

[a] $[U(VI)]_0 = 7.29 \times 10^{-2}\,M$, $[Cr(II)]_0 = 3.00 \times 10^{-2}\,M$, $[H^+]_0 = 2.00\,M$, and ionic strength 2.65; reaction followed at 640 nm. [b] Calculated from $k_4(\text{calcd}) = (kT/h)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT)$ with $\Delta S^* = 21.2 \pm 0.4$ eu and $\Delta H^* = (12.8 \pm 0.1) \times 10^3$ cal mol^{-1}.

Table III. Comparison of the Rates of Decomposition of the $U^V \cdot Cr^{III}$ Complex in H_2O and D_2O[a]

	640 nm		400 nm	
Solvent	ϵ_{int}, M^{-1} cm^{-1}	10^2k, sec^{-1}	ϵ_{int}, M^{-1} cm^{-1}	10^2k, sec^{-1}
D_2O[b]	12.5 ± 0.2	4.91 ± 0.15 (10 runs)	26.9 ± 0.8	5.03 ± 0.20 (8 runs)
H_2O[c]	12.1 ± 0.4	9.05 ± 0.18 (8 runs)	29.4 ± 0.9	8.65 ± 0.22 (5 runs)

[a] $[H^+]_0 = 0.900\,M$, ionic strength 2.65, 30°. [b] $[U(VI)]_0 = 4.68 \times 10^{-2}\,M$, $[Cr(II)]_0 = 2.41 \times 10^{-2}\,M$. [c] $[U(VI)]_0 = 4.86 \times 10^{-2}\,M$, $[Cr(II)]_0 = 2.43 \times 10^{-2}\,M$.

Table IV. Comparison of Observed and Calculated Absorbance for a Typical Run[a]

Time, sec × 10^2	Absorbance (640 nm)		Time, sec × 10^2	Absorbance (640 nm)	
	Obsd	Calcd[b]		Obsd	Calcd[b]
1	0.175	0.177	8	0.287	0.286
2	0.200	0.202	9	0.298	0.294
3	0.220	0.221	10	0.301	0.302
4	0.235	0.237	11	0.309	0.308
5	0.251	0.252	12	0.316	0.314
6	0.264	0.264	13	0.319	0.320
7	0.277	0.276			

[a] $[U(VI)]_0 = 6.30 \times 10^{-3}\,M$, $[Cr(II)]_0 = 3.00 \times 10^{-2}\,M$, $[H^+]_0 = 1.25\,M$, 23.5°, ionic strength 2.00. [b] Calculated by the nonlinear least-squares method described in the text with $k_8 = 1.26 \times 10^4$ M^{-1} sec^{-1} and $k_9 = 5.66 \times 10^2$ M^{-1} sec^{-1}. These values were obtained using a total of 64 time and absorbance readings, only some of which are shown in this table.

The effect of temperature on the rate constant was measured over the range 14-32°, at an acid concentration of 2.00 M and an ionic strength of 2.65. Least-squares analysis of the data (Table II) in terms of the Eyring equation[9] yields values of -21.2 ± 0.4 eu and $(12.8 \pm 0.1) \times 10^3$ cal mol^{-1} for ΔS^* and ΔH^*, respectively.

The rate constant for the decomposition of the $U^V \cdot Cr^{III}$ complex was also measured in D_2O for a solution of 0.90 M H^+ and an ionic strength of 2.65 (Table III). Pooling of the data measured at 400 and 640 nm yielded values of $(4.96 \pm 0.17) \times 10^{-2}$ and $(8.88 \pm 0.20) \times 10^{-2}$ sec^{-1} for the rate constants in D_2O and H_2O, respectively, leading to a value of 1.79 for the ratio $k(H_2O)/k(D_2O)$.

(b) Reaction of Cr(II) with $U^V \cdot Cr^{III}$. As shown in Table IV, the method of calculation of the rate constant for this reaction described above reproduced the observed values of the absorbance at various times very well. In general it was found that the value of k_8 determined in these experiments was somewhat (~15%) lower than those determined previously.[3] However the value of this rate constant was particularly sensitive to variations in the values of ϵ_{int} and in the dead time of the stopped-flow apparatus which was taken as being 7 msec. In contrast, the value of k_9 was not significantly affected by analogous changes in these parameters. This observation is not unexpected since k_8 is considerably greater than k_9 and hence the formation of the intermediate

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(9) S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, pp 195-199.

is essentially complete within a time span not much greater than the dead time of the instrument, particularly for reactions measured in solutions of high ionic strength.[10]

The value of the rate constant k_9 was found to be independent of the initial reagent concentration (Table V) but to increase slightly with increasing acid concentration in the range 0.50-2.00 M H^+. The acid dependency is probably due to a medium effect and can be adequately described by a Harned function (eq 14) with $k_0 = (4.16 \pm 0.15) \times 10^2\ M^{-1}\ sec^{-1}$ and $b = 0.16 \pm 0.02$.

The rate constant of eq 9 was strongly influenced by the ionic strength (adjusted with $NaClO_4$) of the reactant solution, increasing from $(1.06 \pm 0.04) \times 10^2\ M^{-1}\ sec^{-1}$ at an ionic strength of 0.391 to $(3.65 \pm 012) \times 10^2\ M^{-1}\ sec^{-1}$ at an ionic strength of 1.83. The data were found to be adequately described by the extended Debye-Huckel equation (eq 15) with $\Delta Z^2 = 16$, $\log k_0 = (1.48 \pm 0.86) \times 10^{-1}$, $a = 8.5 \pm 0.7$ Å, $C = (7.7 \pm 3.9) \times 10^{-2}$, $A = 0.5070$,[11] and $B = 0.3282$.[11]

The temperature dependency of the reaction was measured over the range 13.5-36.5° and at an acid concentration and ionic strength of 1.25 M and 2.00, respectively (Table VI). Least-squares analysis of the data yielded values of $-(35.2 \pm 1.0)$ eu and $(3.16 \pm 0.30) \times 10^3$ cal mol^{-1} for ΔS^* and ΔH^*, respectively.

(a) Decomposition of the $U^V \cdot Cr^{III}$ Complex. The values of the extinction coefficients of the $U^V \cdot Cr^{III}$ complex at 400 and 640 nm found in this study are in good agreement with those values reported in the two previous studies[1,3] and hence the intermediate exhibiting first-order decay kinetics is the species studied previously.

The first-order rate law observed in this study is consistent with a mechanism in which the dissociation of the complex is the rate-determining step (eq 16), followed by rapid disproportionation of the U(V) so formed (eq 17). Extrapolation of the results obtained from previous studies of the rates of disproportionation of U(V)[12] to the present experimental conditions confirms that the rate constant of reaction 17 exceeds that of reaction 16 by the least three orders of magnitude at temperatures near 30° and at acid concentrations in the range 0.2-2.0 M.

$$U^V \cdot Cr^{III} \xrightarrow{k_{16}} U(V) + Cr(III) \qquad (16)$$

$$2U(V) \xrightarrow{k_{17}} U(IV) + U(VI) \quad \text{(fast)} \qquad (17)$$

A previous, very detailed study[1] of the decomposition of the $U^V \cdot Cr^{III}$ complex at temperatures near 0° showed that under these conditions the mechanism of the reaction was very complex and could not be interpreted in terms of a single reaction. Furthermore, considerable experimental evidence suggested that a second, more reactive intermediate, whose nature could not be elucidated, was also formed in the reactant solution.

To account for the absence of any evidence for these complicating features in our study, the following explanations may be considered.

(i) The formation of the second intermediate is much less significant at the higher temperatures, and any complications resulting from its presence would fall within our experimental error, particularly with respect to the extinction coefficient of the predominant intermediate.

Table V. Effect of Initial Cr(II) and U(VI) Concentrations on the Rate Constant for the Reaction of Cr(II) with $U^V \cdot Cr^{III\,a}$

Run no.	$10^2 \times [U(VI)]_0$, M	$10^2 \times [Cr(II)]_0$, M	No. of determinations	$10^{-2}k_9$, $M^{-1}\ sec^{-1}$
1	0.630	1.50	4	5.12 ± 0.08
	0.630	3.00	4	5.30 ± 0.10
	0.630	4.50	4	5.05 ± 0.12
	0.630	6.00	4	4.83 ± 0.14
	0.630	7.50	4	4.90 ± 0.07
2	1.89	6.00	4	4.78 ± 0.06
	1.57	6.00	4	4.88 ± 0.09
	1.26	6.00	4	5.03 ± 0.11
	0.945	6.00	4	5.20 ± 0.14
	0.630	6.00	4	5.00 ± 0.08
	0.315	6.00	4	5.16 □ 0.07
3	1.26	6.00	4	1.78 ± 0.08
	0.945	6.00	4	1.65 ± 0.09
	0.630	6.00	6	1.68 ± 0.10
	0.315	6.00	4	1.72 ± 0.12
	0.126	6.00	4	1.68 ± 0.08

[a] Conditions: run 1, $[H^+] = 1.00\ M$, 20°, ionic strength 2.00; run 2, $[H^+] = 1.00\ M$, 20°, ionic strength 2.00; run 3, $[H^+] = 0.494\ M$, 20°, ionic strength 0.638.

Table VI. Effect of Temperature on the Rate Constant of the Reaction of Cr(II) with $U^V \cdot Cr^{III\,a}$

Temp, °C	No. of determinations	$10^2 k_9$(obsd), $M^{-1}\ sec^{-1}$	$10^2 k_9$(calcd),[b] $M^{-1}\ sec^{-1}$
13.5	4	4.81 ± 0.10	4.68
18.4	4	5.28 ± 0.09	5.23
20.0	5	5.35 ± 0.12	5.41
23.5	4	5.60 ± 0.09	5.84
28.5	2	6.43 ± 0.08	6.49
33.4	4	7.49 ± 0.11	7.18
36.5	4	7.73 ± 0.16	7.63

[a] Conditions: $[U(VI)]_0 = 6.30 \times 10^{-3}\ M$, $[H^+] = 1.25\ M$, $[Cr(II)]_0 = 3.00 \times 10^{-2}\ M$, ionic strength 2.00. [b] Calculated from $k_9(\text{calcd}) = (kT/h) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$ with $\Delta S^* = -35.2 \pm 1.0$ eu and $\Delta H^* = (3.16 \pm 0.30) \times 10^3$ cal mol^{-1}.

(ii) The second intermediate is at least in part U(V), formed by the dissociation of the major intermediate. This interpretation was considered by Newton and Baker[1] but was rejected partly on the basis of the observation that in the absence of any other added oxidizing agents, the rate of decomposition of the intermediate apparently increases with increasing initial intermediate concentration. However subsequent work[12] has clearly shown that, because of the formation of a $U^V \cdot U^{VI}$ complex, the rate of decay of U(V) is considerably retarded by the presence of excess U(VI) in the reactant solution. This effect complicates the interpretation of the previous results on the decomposition of the intermediate since in this work the intermediate to U(VI) ratio, as well as the intermediate concentration, was varied.

To test this last hypothesis, a computer program to calculate, by the Runge-Kutta method,[5] the concentration of U(V) in the reaction mixture at various times was written. The values of k_{16} and k_{17} required for this program were obtained by extrapolating the results obtained in this study on the decomposition of the intermediate and those previously reported for the disproportionation of U(V)[12] to the appropriate conditions. Two sets of conditions were examined: (a) the effect of increasing the initial $U^V \cdot Cr^{III}$ concentration at 25° and 1 M H^+ and (b) the effect of changing the value of k_{17} at 0.3° and 0.2 M H^+. As the value of k_{17} effectively decreases with increasing U(VI) concentration due to the

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[10] The value of 7 msec for the dead time of the stopped-flow apparatus was the average value determined in the course of the study of the U(VI)-Cr(II) reaction.[3]

[11] R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," 2nd ed, Butterworths, London, 1959, p 392.

[12] T. W. Newton and F. B. Baker, *Inorg. Chem.*, 4, 1166 (1965).

Table VII. Summary of the Rate Laws and Rate Parameters for the Decomposition and Reactions of Some Binuclear Complexes

Reaction	Rate law	ΔH^*, kcal mol^{-1}	ΔS^*, eu	Ref
$Np^V \cdot Cr^{III} \rightarrow Np(V) + Cr(III)$	$R = k[Np^V \cdot Cr^{III}]$	27.7 ± 0.8	8.8 ± 2.8	*a*
$Np^V \cdot Rh^{III} \rightarrow Np(V) + Cr(III)$	$R = k[Np^V \cdot Rh^{III}]$	26.7 ± 0.4	8.6 ± 0.9	*b*
$U^V \cdot Cr^{III} \rightarrow U(V) + Cr(III)$	$R = k[U^V \cdot Cr^{III}]$	12.8 ± 0.1	-21.2 ± 0.4	*c*
$V^{III} \cdot Cr^{III} \rightarrow V(III) + Cr(III)$	For the complex, $k(\text{obsd}) = (k_0 Q + k_1[H^+])/(Q + [H^+])$			*d*
	k_0	14.6 ± 0.8	-17.6 ± 2.6	
	k_1	14.0 ± 0.2	-12.3 ± 0.7	
$Pu^V \cdot Cr^{III} + Pu(III) \rightarrow 2Pu(IV) + Cr(III)$	$R = k[Pu^V \cdot Cr^{III}][Pu(III)]$	4.58 ± 0.07	-33.6 ± 0.2	*e*
$U^V \cdot Cr^{III} + Cr(II) \rightarrow U(IV) + 2Cr(III)$	$R = k[U^V \cdot Cr^{III}][Cr(II)]$	3.16 ± 0.30	-35.2 ± 1.0	*c*

[a] J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964). [b] R. K. Murmann and J. C. Sullivan, *ibid.*, **6**, 892 (1967). [c] This work. [d] J. H. Espenson, *Inorg. Chem.*, **4**, 1533 (1965). [e] C. Lavallee and T. W. Newton, *ibid.*, **11**, 2616 (1972).

formation of the $U^V \cdot U^{VI}$ complex,[12] the latter condition simulates the effect of changing U(VI) concentration at constant initial $U^V \cdot Cr^{III}$ concentration.

The results obtained (Figure 3A) show that under otherwise constant conditions, the maximum concentration of U(V) relative to the initial $U^V \cdot Cr^{III}$ concentration *increases* with decreasing initial $U^V \cdot Cr^{III}$ concentration. This unusual effect arises because the decomposition of the intermediate is a first-order process while the disproportionation of U(V) is a second-order process and thus the rate of the latter reaction is very sensitive to the concentration of U(V). Since the present study on the decomposition of the $U^V \cdot Cr^{III}$ complex was carried out using high ($>2.0 \times 10^{-2}$ *M*) initial concentrations, the above calculations show that the maximum concentration of U(V) in the reactant solution would not exceed 5% of the initial complex concentration. By contrast, if initial complex concentrations of $<2 \times 10^{-3}$ *M* are used, the U(V) will reach a value of 20% of the initial complex concentration.

The results also show (Figure 3B) that the maximum U(V) concentration in the reactant solution increases with decreasing values of k_{17} or (*vide supra*) with increasing U(VI) concentration. For example, the value of k_{17} at 0°, 0.2 *M* H^+, and 1.6×10^{-2} *M* U(VI) is 10 M^{-1} sec^{-1}, and if an initial $U^V \cdot Cr^{III}$ concentration of 2×10^{-3} *M* is chosen, the maximum U(V) concentration in the reactant solution will be as high as $\sim 0.8 \times 10^{-3}$ *M* or ~40% of the initial $U^V \cdot Cr^{III}$ concentration.

The preceding calculations will clearly be applicable to the actual conditions only if the reaction between U(V) and the $U^V \cdot Cr^{III}$ intermediate is slow compared to the normal disproportionation reaction of U(V) ions. Some experimental results in support of this assumption have been reported,[1] although the validity of this result has recently been questioned.[13] The above calculations thus do not conclusively prove that the second intermediate postulated by the previous workers[1] can be identified as either U(V) or a $U^V \cdot U^{VI}$ complex. It is clear, however, that any effects due to the presence of U(V) ions would be most noticeable under conditions of low initial $U^V \cdot Cr^{III}$ concentrations and under conditions where the U(VI) concentration is high. In this respect it is of interest to recall that the results obtained by previous workers[1] on the decomposition of the intermediates in the absence of any added oxidizing agents do appear to show that the rate of decomposition of the intermediate decreases with increasing U(VI) concentration.

Table VII summarizes the rate laws and rate parameters of a series of reactions involving the decomposition of binuclear complexes. The difference in the rate parameters of the $U^V \cdot Cr^{III}$ complex and those obtained for the two Np(V) species is quite striking and suggests that the mechanism for the dissociation of the U(V) complex is different from that of the two Np(V) species. A comparison between the rate parameters for the dissociation of the $V^{III} \cdot Cr^{III}$ and $U^{IV} \cdot Cr^{III}$ species shows that these are similar but the acid dependency term in the rate law for the decomposition of the former species suggests a major difference in the reactions of the two complexes.

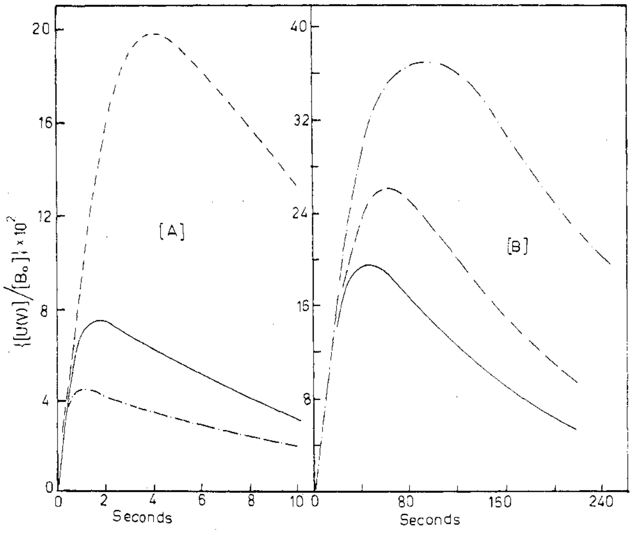

Figure 3. Calculated time dependency of the U(V) concentration (expressed as a percentage of the initial $U^V \cdot Cr^{III}$ concentration) in the reactant solution during the decomposition of the $U^V \cdot Cr^{III}$ complex. [A] $k_{16} = 0.1$ sec^{-1}, $k_{17} = 700$ M^{-1} sec^{-1}, and values of B_0 (initial $U^V \cdot Cr^{III}$ concentration) are 2×10^{-3}*M* (– – –), 2×10^{-2} *M* (——), and 6×10^{-2} *M* (– · – · –). [B] $k_{16} = 0.009$ sec^{-1}, $B_0 = 2 \times 10^{-3}$ *M*, and values of k_{17} are 60 M^{-1} sec^{-1} (——), 30 M^{-1} sec^{-1} (– – –), and 10 M^{-1} sec^{-1} (– · – · –).

Sullivan[14] has pointed out that the rate-determining step in the decomposition of these complexes can be either the dissociation of the complex (SN1 mechanism) or the addition of a molecule of water to the complex to form a seven-coordinate intermediate (SN2 mechanism). If the reactions proceed by an SN2 mechanism, it might perhaps be expected that the rate parameters for the decomposition of the Np(V) and U(V) complexes would be more alike than they are in fact observed to be. On the other hand, the isotope effect observed for the decomposition of the $U^V \cdot Cr^{II}$ complex suggests that a water molecule does take part in the reaction,

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(13) T. W. Newton, personal communication.

(14) J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964).

but solvent isotope effects of this type are frequently difficult to interpret with confidence.

One plausible interpretation of the marked difference between the rate parameters of the decomposition of the $U^V\cdot Cr^{III}$ complex and those of the two Np(V) complexes is that it indicates the importance of the f electrons in the bonding of these species. It may be noted that replacing Cr(III) (a 3d ion) by Ru(III) (a 4d ion) in the Np(V) complex has little effect on the magnitude of the rate parameters. However, replacing the $5f^2$ Np(V) ion by the $5f^1$ U(V) ion has a marked effect on the kinetic behavior.[15] A study of the rates of decomposition of the analogous $Pu^V\cdot Cr^{III}$ complex would clearly be of considerable interest in this respect.

(b) **Reaction of Cr(II) with $U^V\cdot Cr^{III}$.** The results obtained for this reaction support the conclusion of Gordon[2] that the intermediate reacts with excess Cr(II) before either disproportionating or dissociating.

Although the net reaction (eq 3) requires the consumption of four protons for each molecule of $U^V\cdot Cr^{III}$ reduced, the rate law for the reduction of $U^V\cdot Cr^{III}$ does not contain any acid concentration term. Analogous results have been obtained for the reduction of the $Pu^V\cdot Cr^{III}$ complex by Pu(III)[16] and Fe(II)[17] and since the rate laws for the disproportionation or reduction of the actinide(V) ions usually contain a positive acid dependency, it has been suggested[17] that the Cr(III) ion plays a role similar to that of the proton in the reduction mechanism. This conclusion is supported by the observation that the reduction of $Pu^V\cdot Cr^{III}$ by either Pu(III) or Fe(II) is much faster than the reduction of uncomplexed Pu(V) by these reagents. Unfortunately the rate constant for the reduction of uncomplexed U(V) by Cr(II) cannot easily be determined, but preliminary experiments suggest that the reduction of U(V) by Eu(II), which has virtually the same redox potential as Cr(II), is much slower than the disproportionation of U(V) in 1 M $HClO_4$ at 20°.[18] It would thus appear that the general mechanism of the reduction of $U^V\cdot Cr^{III}$ by Cr(II) is similar to that operating in the reduction of the $Pu^V\cdot Cr^{III}$ complex.

The lack of an acid dependency in the rate law also indicates that the major activation process is the reaction

$$\mathrm{Cr(II)} + \mathrm{U^V\cdot Cr^{III}} \rightarrow [\mathrm{Cr\cdots O\text{-}U\text{-}O\cdots Cr}]^* \tag{18}$$

where the activated complex may well have a linear structure as suggested by Gordon.[2] However, the possibility that the perchlorate ion may be involved in the formation of the activated complex cannot be entirely excluded.

Comparison of the rate parameters of the $U^V\cdot Cr^{III}$–Cr(II) and $Pu^V\cdot Cr^{III}$–Pu(III) reactions (Table VII) shows that the higher rate for the former reaction is almost entirely the result of a slightly smaller ΔH^* value, the ΔS^* values being nearly the same for the two reactions. For a series of similar reactions it is frequently found that the ΔS^* value becomes more negative as the charge on the activated complex increases.[19] It would thus be expected that the ΔS^* value for the Cr(II)–$U^V\cdot Cr^{III}$ reaction would be less negative compared to that found for the Pu(III)–$Pu^V\cdot Cr^{III}$ reactions. The observation that the two values are in fact almost identical could indicate that the $[\mathrm{Cr\cdots O\text{-}U\text{-}O\cdots Cr}]^*$ activated complex has a higher charge density when compared to the one formed in the Pu(III)–$Pu^V\cdot Cr^{III}$ reaction.

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Registry No. Uranium(VI), 22541-40-8; chromium(II), 22541-79-3.

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(15) The author wishes to thank Dr. J. C. Sullivan for suggesting this interpretation of the results.

(16) C. Lavallee and T. W. Newton, *Inorg. Chem.*, **11**, 2616 (1972).

(17) T. W. Newton and M. J. Burkhart, *Inorg. Chem.*, **10**, 2323 (1971).

(18) A. Ekstrom, unpublished data; see also ref 12.

(19) (a) J. Halpern, *Quart. Rev., Chem. Soc.*, **15**, 220 (1961); (b) T. W. Newton and F. B. Baker, *Advan. Chem. Ser.*, No. 71, 268 (1967).

Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174

Mechanism of the Reduction of Bromate Ion by Hexacyanoferrate(II) and by Bromide Ion in Acidic Aqueous Solution

JAMES P. BIRK* and STEPHEN G. KOZUB

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The reaction between ferrocyanide and bromate ions follows partially autocatalytic kinetics, with the autocatalysis arising from the bromide–bromate reaction. The rate equation is given by $-d[\mathrm{Fe(CN)_6}^{4-}]/dt = 6k_1[\mathrm{Fe(CN)_6}^{4-}][\mathrm{BrO_3}^-] + 6k_3[\mathrm{Br}^-][\mathrm{BrO_3}^-][\mathrm{H}^+]^2$, with $k_1 = c + d[\mathrm{H}^+]^2$. Values of the parameters at 25.0° and 0.50 M ionic strength are $c = (1.25 \pm 0.12) \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, $d = 0.193 \pm 0.005\ M^{-3}\ \mathrm{sec}^{-1}$, and $k_3 = 2.86 \pm 0.06\ M^{-3}\ \mathrm{sec}^{-1}$. A detailed mechanism is presented to explain these results.

Introduction

The rates of both oxygen exchange and oxidation–reduction reactions of many oxy anions depend very strongly on acid concentration. For a number of oxy anions (*e.g.*, SO_4^{2-}, NO_3^-, ClO_3^-, BrO_3^-, CO_3^{2-}, and NO_2^-) the rate laws for oxygen exchange and for reduction by a species R generally have major rate terms of the form $k[XO_m{}^{n-}][H^+]^2$ and $k[XO_m{}^{n-}][R][H^+]^2$, respectively. On the basis of close correlations between rates of exchange and redox reactions as well as other evidence (*e.g.*, isotope effects) which has been discussed extensively elsewhere,[1,2] it has been proposed

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* Author to whom inquiries should be addressed at the Department of Chemistry, Arizona State University, Tempe, Ariz. 85281.