decrease in the stoichiometric ratio to close to 1 in the presence of phenol. The reactions with phenol, chloride, and bromide ions show the same trends at the different hydrogen ion concentrations shown in Tables IX and X as they did in 0.60 *M* $HClO_4$.

It is also interesting to note that the maximum in the $[Cl(III)]/[U(IV)]_{consumed}$ ratio occurs at the same starting ratios of $[Cl(III)]/[U(IV)]$ under all three hydrogen ion concentrations studied (0.18, 0.60, and 1.50 *M*), which suggests that the rate-determining steps are independent of the hydrogen ion concentration.

In an attempt to verify the mechanism shown in eq. 5 and 6, it was shown that ClO_2^- oxidizes U(IV) more rapidly than Cl_2, OCl^-, or ClO_2. In order for the ClO_2 to play a major role, it would have to be produced and oxidize the U(IV) much more rapidly than does the ClO_2^-. Neither of these situations is true.

A series of similar kinetic experiments was carried out by following the concentration of U(IV) spectrophotometrically. The oxidizing agents used were ClO_2, ClO_2^-, and OCl^- at 0 and 25°. Stoichiometry appropriate to the observed results was used for calculation of the kinetic data. However, it should be noted that changes in assumed stoichiometry did not markedly effect the linearity of the second-order rate equation and the rate constants were only slightly altered by these changes. The apparent second-order rate constants for the uranium(IV)–halogenate reaction with Cl(III), Cl(IV), and Cl(I) are shown in Table XI.

TABLE XI

SECOND-ORDER RATE CONSTANTS FOR URANIUM(IV)–HALOGENATE REACTION

[U(IV)], *M*	Halogen	[H⁺], *M*	Temp., °C.	k,[a] M^{-1} sec.$^{-1}$
0.0387	0.0297 *M* Cl(III)	0.25	0	4.6
0.0194	0.0297 *M* Cl(III)	0.25	0	4.0
0.0387	0.0297 *M* Cl(III)	0.25	25	22
0.0387	0.0297 *M* Cl(III)	1.30	25	18
0.0387	0.0323 *M* Cl(IV)	0.25	25	6.5
0.0304	0.0339 *M* Cl(I)	0.25	25	4.1

[a] Apparent second-order rate constant.

Uranium(IV) was most rapidly oxidized by ClO_2^- under all conditions. The relative rates of reactions between U(IV) and various halogenates were $ClO_2^- > ClO_2 > OCl^- > Cl_2 > ClO_3^-$.

It should be noted that very little if any effect occurs with a 5-fold change in the hydrogen ion concentration in the apparent second-order rate constant for the U(IV)–Cl(III) reaction.

Thus, the rate law for the reaction between uranium(IV) and chlorine(III), in agreement with eq. 5 proposed from the stoichiometric results, does not appear to show any hydrogen ion dependence. This suggests that the activated complex for the rate-determining step most probably contains the species ClO_2^- and U^{4+} or $HClO_2$ and UOH^{3+}. The details of a complete kinetic study of the reaction between uranium(IV) and the various chlorine-containing halogen species as a function of hydrogen ion concentration, added salts, and temperature will be discussed elsewhere.

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The Oxidation of Aqueous Uranium(IV) by Bromine

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The reaction between uranium(IV) and bromine has been studied in 0.7 to 2.0 *M* perchloric acid at 25°. The value of the rate constant appropriate to the rate law

$$-d[U(IV)]/dt = k[U(IV)][Br_2][H^+]^{2-}$$

was found to be 5.3×10^{-4} *M* sec.$^{-1}$. The reaction was markedly catalyzed by Fe(III). Possible mechanisms consistent with the observed rate law are proposed.

The preliminary studies by Gordon and Kern[1] on the reactions of uranium(IV) and various halogenates suggested that the reaction between uranium(IV) and bromine proceeded *via* a single two-electron path involving the direct oxidation of U(IV) to UO_2^{2+} and the reduction of Br_2 to $2Br^-$. It is apparent from the stoichiometry of the reaction

$$Br_2 + U(IV) + 2H_2O \longrightarrow UO_2^{2+} + 2Br^- + 4H^+$$

that the concentration of hydrogen ion increases as the reaction proceeds and the change of proton activity during the reaction could affect the rate. Since it is difficult to buffer perchlorate solutions without the addition of complexing ligands, it was convenient to work in an acidity range (0.5–2.0 *M*) which minimized any changes in hydrogen ion concentration.

Tetravalent uranium in solution shows a marked

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[1] D. M. H. Kern and G. Gordon in "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, New York, N. Y., 1964, p. 655.

tendency toward complex ion formation. A number of these complexes have been investigated in perchloric acid solution. Ahrland and Larrson,[2] by using measurements of the UO_2^{2+}–U(IV) couple, have found that U(IV) will form weak complexes with chloride and bromide in 1 *M* sodium perchlorate at 20°. They have represented the formation of the bromide complex by the equilibrium $U^{4+} + Br^- = UBr^{3+}$. The constant was found to be 1.5 M^{-1}.

In strongly acid solution there is little doubt that uranium(IV) exists as the species U_{aq}^{4+}.[3–5] Hietanen has studied the hydrolysis of uranium(IV) in 3 *M* perchlorate medium at 25.0° by means of electrometric titration. The results are interpreted in terms of the equilibrium $U_{aq}^{4+} \rightleftarrows UOH^{3+} + H^+$. The hydrolysis constant was found to be 1.0×10^{-2} under these conditions. In solutions of low acidity chain-like complexes are postulated to account for the higher hydrolyzed species.

The formation of U(V) in solutions of U(IV) and UO_2^{2+} has been demonstrated by Heal[6] in accordance with the equilibrium

$$2UO_2^+ + 4H^+ = UO_2^{2+} + U^{4+} + 2H_2O \qquad (1)$$

The formula, UO_2^+, for the uranium(V) ion in acid solutions has been deduced on the basis of detailed polarographic studies.[7,8] Nelson and Kraus[9] have quantitatively studied the uranium(IV)–(V)–(VI) equilibrium in perchlorate media; they report that the stability of the UO_2^+ ion increases with decreasing acidity. The optimum stability range is from pH 2.5 to 3.0. They also reported equilibrium constants for the disproportionation of UO_2^+ into UO_2^{2+} and U^{4+} over a range of ionic strength. The value for K_{eq} increases

$$K_{eq} = \frac{[UO_2^{2+}][U^{4+}]}{[UO_2^+]^2[H^+]^4}$$

with increasing ionic strength. At zero ionic strength the constant has a value of 1.7×10^6.

The kinetics of the disproportionation of UO_2^+ has been studied by Kern and Orlemann,[10] Imai,[11] Gordon and Taube,[12] and Masters and Schwartz.[13]

The rate law

$$-d(UO_2^+)/dt = k[H^+][UO_2^+]^2$$

indicates a decrease in kinetic stability with increasing acidity and the value of the specific rate constant increases with increasing ionic strength.

Experimental

The water used throughout the experimental work was distilled in an all-metal Barnsted still and passed through an Illco-Way Research-Model exchange column.

Uranyl perchlorate was prepared from Mallinckrodt analytical reagent $UO_2(NO_3)_2 \cdot 6H_2O$ by two different methods. In the first method, concentrated perchloric acid was added to a solution of $UO_2(NO_3)_2$ which was fumed to remove the nitric acid. This procedure was repeated several times. A portion of the resulting uranyl perchlorate was tested to detect the presence of nitrate. The concentration of nitrate was shown to be less than 2×10^{-5} *M* by using the diphenylamine test.

In the second method, hydrogen peroxide was added with constant stirring to a dilute solution of uranyl nitrate to precipitate uranyl peroxide. The yellow solid was filtered and washed with distilled water to remove nitrate and excess peroxide. The uranyl peroxide was thermally decomposed to uranium trioxide at 250°.[14] Completeness of decomposition was verified by adding a small sample to 0.4 *M* perchloric acid. Uranium trioxide dissolves readily but uranium peroxide is only slightly soluble. The uranyl perchlorate was prepared by dissolving the uranium trioxide in a slight excess of perchloric acid. The resulting uranyl perchlorate was purified by three recrystallizations.

Uranium(VI) was reduced to U(IV) by electrolysis by using a vigorously stirred mercury cathode and a gauze platinum anode. A potential difference of −0.3 volt *vs.* s.c.e. was maintained. Provided the solution was kept cold, the reaction went to completion with no formation of U(III) or chloride. The total uranium content and acidity of the stock U(IV) solution was determined by using techniques described elsewhere.[1,15]

Sodium perchlorate was prepared by neutralizing reagent grade sodium carbonate with perchloric acid. The calculated amount of acid required for complete neutralization was added slowly to a rapidly stirred slurry of sodium carbonate in water. The solution was filtered through a sintered glass funnel, acidified slightly, and boiled to expel carbon dioxide. Solid sodium perchlorate was obtained by partial crystallization followed by three recrystallizations. The acid content of the solutions was determined by titrating an aliquot directly with sodium hydroxide using phenolphthalein as the indicator. A second aliquot was then passed through a Dowex-50 exchange column to determine the total cation concentration. The concentration of the sodium ion was taken as the difference between the total cation concentration and the hydrogen ion concentration.

Aqueous solutions of bromine were prepared by adding Dow purified grade bromine to water. The solution was shaken vigorously for approximately 5 min. The stock solutions were standardized by adding an aliquot to excess sodium iodide in 0.1 *N* acid and followed by titration with 0.1 *N* standard sodium thiosulfate by using starch as the indicator. The bromine solutions were prepared immediately before each kinetic run. The stock liquid bromine was stored in a glass separatory funnel to prevent contamination from the lead stopper of the original container.

The principal method of analysis used for the kinetic studies was the spectrophotometric determination of U(IV) at 6484 Å. by using a Cary Model 14 double beam recording spectrophotometer. The temperature in both compartments of the spectrophotometer was controlled at 25.0° by means of water circulated from a constant temperature bath.

The reactions were initiated by injecting a known volume of standardized U(IV) solution into a 25-ml. volumetric flask filled to the mark with the desired amounts of bromine water, perchloric acid, sodium perchlorate, sodium bromide, and distilled water. Mixing was accomplished by means of a small magnetic stirrer in the volumetric flask. After complete mixing, an aliquot was transferred to a spectrophotometric cell and placed in the sample compartment of the spectrophotometer, and the cells were tightly stoppered with ground glass stoppers. The first absorbance reading was usually taken in less than 60 sec. after mixing.

The uranium was forcibly injected into the bromine solutions by means of a Krough-Keys syringe pipet equipped with a 2-cc. standard lever syringe. A polyethylene tip was used on the syringe instead of a normal stainless steel hypodermic needle to pre-

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vent contamination which might result from bromine or acid attack of the stainless steel. The syringe was calibrated to deliver a specific volume of liquid by filling it with water and by weighing the amount of water delivered. The reproducibility of delivery was found to be ±0.2%. Before each run, the syringe was filled with uranium(IV) solution and brought to thermal equilibrium. The volumetric flask containing bromine solution was also thermally equilibrated. The solutions were then mixed and transferred to a spectrophotometric cell.

The mixing time with this procedure was determined by adding acid and indicator to a 25-ml. volumetric flask and diluting to the mark. Approximately 5% excess sodium hydroxide was then injected by means of the syringe. The time required for even distribution of the indicator color was less than 15 sec.

Results

A detailed spectrophotometric study of uranium(IV) was carried out to determine the effect of UO_2^{2+}, Br^-, and H^+ on the U(IV) spectra. It has been reported that U(V) cannot have an extinction coefficient greater than 1.5 in this region.[9] The maximum absorption band of U(IV) at 6484 Å. was the most favorable wave length at which to study the kinetics of the U(IV)–Br_2 reaction with ≈ 0.01 *M* U(IV), and at this wave length U(VI), Br_2, and Br_3^- are almost completely transparent.

The molar extinction coefficient, ϵ, at 6484 Å. of uranium(IV) was evaluated to be 60.00 M^{-1} over the entire experimental range of acidity. The magnitude and constancy of ϵ compare favorably with the results of Nelson and Kraus.[9] A final series of spectrophotometric experiments in which all the components were present in concentrations similar to those used in the kinetic studies confirmed that U(IV) is the only absorbing species at 6484 Å.

Since the preliminary results of Gordon and Kern had indicated that the oxidation of U(IV) by Br_2 followed over-all second-order kinetics, the initial kinetic data obtained by titrimetric techniques were analyzed by using the integrated second-order expression

$$kt = \frac{1}{[a-b]} \ln \frac{[b(a-x)]}{[a(b-x)]}$$

where *a* is the concentration of uranium(IV) and *b* is the concentration of bromine, and $(a - x)$ and $(b - x)$ are the concentrations of uranium(IV) and bromine at any time, *t*.

A graph of

$$\frac{1}{[a-b]} \ln \frac{[b(a-x)]}{[a(b-x)]}$$

as a function of time should be linear. The value of the rate constant *k* can be obtained from the slope of the line. All of the titrimetric data showed considerable deviation from linearity after 50% of the reaction was completed and the values of *k* obtained from the initial slopes were nonreproducible in the absence of bromide ion.

A spectrophotometric kinetic study was made to determine the U(IV) dependence under conditions of tenfold excess Br_2. The linearity of a graph of log [U(IV)] as a function of time appears to confirm the observations of Kern and Gordon. Other calculations were made by assuming three-halves- and second-order U(IV) dependence. These were unsatisfactory.

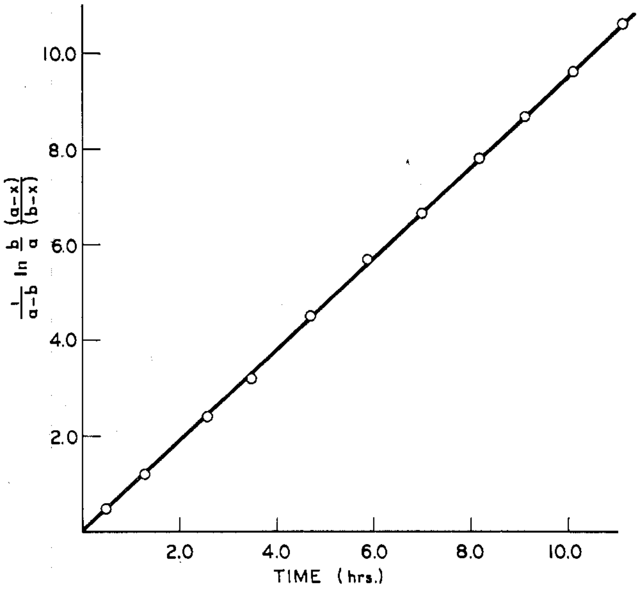

Fig. 1.—Typical second-order rate law plot for the uranium(IV)–bromine(0) reaction.

A second series of spectrophotometric kinetic experiments was made to determine whether the reaction followed total second-order kinetics, first with respect to each component with 0.3 *M* NaBr and 0.7 *M* $HClO_4$ present initially. The data were treated by means of the second-order rate expression. The calculations were made on an I.B.M. 1620 computer by calculating the values of ln $[b(a - x)/a(b - x)]$ and then the best straight line was found by the method of least squares. These data are summarized in Table I. All of the second-order plots were linear for at least 80% of the reaction and the values of the rate constants in Table I confirm second-order dependence. A graph of a set of typical rate data is shown in Fig. 1.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE U(IV)–Br_2 REACTION

$[H^+] = 0.70\ M$, $[Br^-] = 0.300\ M$, $I = 3.00\ M$

[U(IV)], *M*	C_{Br_2},[a] *M*	$k \times 10^3$, M^{-1} sec.$^{-1}$	$k_1 \times 10^4$, *M* sec.$^{-1}$
0.009292	0.07000	1.14	5.55
0.09267	0.06307	1.11	5.44
0.010225	0.06574	1.17	5.69
0.010225	0.05598	1.18	5.74
0.01437	0.05078	1.12	5.47

[a] C_{Br^2} is defined as $[(Br_2) + (Br_3^-)]$.

It was necessary to investigate the effect of bromide and UO_2^{2+} on the rate of the reaction. Tables II and III show the effect on the rate when bromide and UO_2^{2+} are initially added to the reaction mixture.

An examination of the data in Table II reveals a possible trend in experiments 1, 2, 4, and 5. There is approximately a 10% increase in the rate constant when the bromide ion concentration is varied from 0.025 to 0.200 *M*. It should be pointed out that the relative amount of bromine present as tribromide increases from ~0.2 to ~0.8 for the change of bromide ion concentration from 0.025 to 0.200 *M*. The change in the value of the rate constant is seen to be reasonably small relative to the large change in bromide and tribromide ion concentrations. This change in the rate constant could easily be due to the Br^- complexing of U^{4+} or possibly due to medium effects. In light of the difficulty in the over-all reproducibility of the data, possibly due to the volatility of aqueous bromine or trace metal ion contamination, it is difficult to ascertain the effect of the bromide ion to a greater precision than is reported in Table II.

TABLE II

DEPENDENCE OF THE RATE ON THE INITIAL CONCENTRATION OF BROMIDE ION

$[H^+] = 0.70\ M, I = 3.00\ M$

$[Br^-]$, *M*	[U(IV)], *M*	C_{Br_2}, *M*	$k \times 10^3$, M^{-1} sec.$^{-1}$	$k_1 \times 10^4$, *M* sec.$^{-1}$
0	0.01016	0.07347	0.99	4.8_3
0.025	0.01033	0.07245	1.07	5.2_4
0.050	0.01019	0.06602	1.13	5.4_9
0.100	0.01043	0.06863	1.10	5.3_8
0.200	0.01026	0.05564	1.20	5.8_6
0.300	0.00926	0.06307	1.11	5.4_4
0.400	0.01031	0.06082	1.11	5.4_4

The data in Table III indicate that the addition of UO_2^{2+} to the reaction has little detectable effect on the rate of oxidation of U(IV) in the presence of 0.300 *M* Br^- and that the species Br_2 and Br_3^- react with U(IV) with essentially the same rate.

TABLE III

DEPENDENCE OF THE RATE ON THE INITIAL CONCENTRATION OF URANYL ION

$[H^+] = 0.70\ M, [Br^-] = 0.300\ M, I = 3.00\ M$

$[UO_2^{2+}]$, *M*	C_{Br_2}, *M*	[U(IV)], *M*	$k \times 10^3$, M^{-1} sec.$^{-1}$	$k_1 \times 10^4$, *M* sec.$^{-1}$
0	0.0700	0.00932	1.12	5.4_4
0	0.03528	0.01161	1.09	5.3_3
0.050	0.02965	0.01108	1.11	5.4_4
0.100	0.03421	0.01502	1.22	5.9_4
0.300	0.06574	0.01023	1.17	5.6_9
0.300	0.06307	0.00927	1.11	5.4_4

Two series of experiments were made to determine the effect of hydrogen ion. One series without any UO_2^{2+} initially added and the second series with the initial UO_2^{2+} concentration 0.300 *M*. The results are summarized in Table IV.

The data in Table IV show a definite hydrogen ion dependence. The rate law can be rewritten in the form

$$\text{rate} = k[U(IV)][Br_2] = k_1[U(IV)][Br_2][H^+]^{-2}$$

and the values of k_1 are shown in Tables I–IV. The average value of k_1 is $5.3 \pm 0.3 \times 10^{-4}\ M$ sec.$^{-1}$.

Since it has been demonstrated that dissolved oxygen may affect various U(IV) reactions, this effect has been investigated in this system. Experiments were made in which all the reactants were deaerated with N_2 and the rate constants compared with those in which no precautions were taken to remove air. The data are summarized in Table V. Experiments in which oxygen-saturated solutions were used deviated from the normal second-order kinetics due to the oxidation of uranium(IV) by the large amount of dissolved O_2. No such deviations were observed with the normal solutions. It appears that dissolved oxygen from air has little significant effect on the rate of the reaction.

TABLE IV

DEPENDENCE OF THE RATE ON THE HYDROGEN ION CONCENTRATION

$[Br^-] = 0.300\ M, I = 3.00\ M$

[U(IV)], *M*	C_{Br_2}, *M*	$[H^+]$, *M*	$k \times 10^3$, M^{-1} sec.$^{-1}$	$k_1 \times 10^4$, *M* sec.$^{-1}$
0.01161	0.03309	2.00	0.135	5.3_8
0.01161	0.03426	1.50	0.234	5.2_7
0.01161	0.03306	1.20	0.383	5.5_2
0.01161	0.03528	0.70	1.09	5.3_6
0.01161	0.03471	0.50	1.72	4.3_0
0.00947[a]	0.06282	1.40	0.262	5.1_3
0.00982[a]	0.05962	1.02	0.369	3.8_3
0.00988[a]	0.05843	0.900	0.502	4.0_8
0.01026[a]	0.05831	0.800	0.861	5.4_9
0.01102[a]	0.05882	0.600	1.32	4.7_4

[a] 0.300 *M* UO_2^{2+} added.

TABLE V

EFFECT OF DISSOLVED OXYGEN ON THE RATE

[U(IV)], *M*	C_{Br_2}, *M*	Conditions	$k \times 10^3$, M^{-1} sec.$^{-1}$
0.00929	0.07000	Deaerated	1.08
0.00933	0.07000	Deaerated	1.12
0.00927	0.06307	Normal	1.11
0.01022	0.06574	Normal	1.17

It has been shown that U(IV) can interact with UO_2^{2+} to form the very reactive species U(V). Furthermore, in perchlorate solutions of U(IV) and UO_2^{2+}, ultraviolet radiation slightly increases the steady-state concentration of U(V).[8,13] This effect was investigated in this system by exposing solutions from identical reaction mixtures to high intensity infrared, fluorescent, and tungsten light; the rates were compared to that of a reaction made in the complete absence of light. There was no significant difference in the rates of the reaction.

The rate of the oxidation of U(IV) has frequently been reported to be affected by low concentrations of various ionic species.[16,17] This effect was studied in this system by adding the perchlorate salts of Pb(II), Cu(II), Ni(II), Fe(III), Mn(II), Co(II) and the sodium salts of F^- and Cl^-. It was found that the 0.001 *M* Fe(III) and the 0.001 *M* Mn(II) profoundly increase the rate of disappearance of U(IV). For example, a solution initially containing 0.0116 *M* U(IV), 0.0342 *M* Br_2, 0.300 *M* Br^-, 0.70 *M* $HClO_4$ (and made up to an ionic strength of 3.00 with $NaClO_4$), and 0.001 *M* Fe(III) was more than 90% complete in less than 60 sec. The other added ions had little or no effect on the rate of the reaction.

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Discussion

Under the experimental conditions employed, the only oxidizing species of importance are Br_2 and Br_3^-. Although OBr^-, HOBr, BrO_3^-, and O_2 can exist, it can be shown that these oxidizing agents are not consistent with the measured rate law.

For example, the species OBr^- is capable of oxidizing U(IV). The concentration of OBr^- in solution is dependent upon the hydrogen ion concentration and the bromide concentration. The concentration of OBr^- in the most favorable circumstances approaches 10^{-17} *M* in this study. The magnitude of the OBr^- concentration is enough in itself to discourage any attempt to justify it as contributing significantly to the oxidation of U(IV).

The principal U(IV) species existing in the acid region 0.7–2.0 *M* is undoubtedly the quadrivalent uranium ion, U_{aq}^{4+}. However, small concentrations of hydrolyzed U(IV) species are present. In addition, small concentrations of UO_2^+ are formed when U(IV) and U(VI) are present in the same solution.

Many investigators have postulated mechanisms of U(IV) oxidation–reduction reactions in which the species U(V) is a reactive intermediate.[16,17] The main evidence supporting a U(V) intermediate has been based on the catalytic effect of various cations and anions on the rate and the catalytic effect of light, which are known to increase the steady-state concentration of U(V). Since UO_2^{2+}, various cations such as Cu^{2+}, Ni^{2+}, and Co^{2+}, and high intensity light did not noticeably affect the rate of the reaction, it was concluded that the principal path for the reaction does not proceed through a uranium(V) intermediate.

Therefore, a possible mechanism involves a two-electron transfer between U(IV) and Br_2. In addition, the formation of the activated complex involves the loss of two protons, presumably by the formation of the species $U(OH)_2^{2+}$. Thus

$$U_{aq}^{4+} = U(OH)_2^{2+} + 2H^+ \qquad (2)$$

$$U(OH)_2^{2+} + Br_2 =$$
$$U(OH_2)^{4+} + 2Br^- \quad \text{rate-determining} \qquad (3)$$

$$U(OH)_2^{4+} = UO_2^{2+} + 2H^+ \qquad (4)$$

is consistent with the experimental data.

Previous investigators[18,19] have concluded that dissolved bromine is usually more reactive than the tribromide ion. However, the lack of dependence of the rate on the bromide ion concentration as the relative amount of bromine present as tribromide changes from ∼0.2 to ∼0.8 indicates that dissolved bromine and tribromide ions react with essentially the same rates.

The mechanism proposed is not intended to preclude other possible mechanisms such as

$$Br_2 + U(OH)_2^{2+} =$$
$$Br_2^- + UO_2^+ + 2H^+ \quad \text{rate-determining} \qquad (5)$$

$$Br_2^- + UO_2^+ = 2Br^- + UO_2^{2+} \qquad (6)$$

$$Br_2^- + U(OH)_2^{2+} = UO_2^+ + 2Br^- + 2H^+ \qquad (7)$$

in which the UO_2^+ might disproportionate to give UO_2^{2+} and U^{4+} as shown in eq. 1. In the absence of direct evidence for UO_2^+ as an intermediate and the inertia of the rate of the reaction to various regents reported to influence the concentration of UO_2^+, the former mechanism may be a better choice.

The catalysis of Fe(III) can easily be explained in terms of the following.

$$2Fe(III) + U(IV) = 2Fe(II) + UO_2^{2+} \quad \text{rapid} \qquad (8)$$

$$2Fe(II) + Br_2 = Fe(III) + 2Br^- \quad \text{rapid} \qquad (9)$$

This catalyzed reaction is supported by the fact that reactions 8 and 9 are qualitative reactions routinely used in analytical chemistry at room temperature. No simple explanation of this type appears to be available for the Mn(II) catalysis since the oxidation potential for Mn(II) is probably more negative than −1.5 v.

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