

the expected coordination through S. Metal complexes of dithiooxalate¹² were reported to show a strong band at 1600 cm.⁻¹ (C=O stretch) and two bands at about 1080 and 940 cm.⁻¹ assigned to a coupled C-C and C-S stretching vibration and a coupled C-S stretching and

(12) J. Fujita and K. Nakamoto, *Bull. Chem. Soc. Japan*, **37**, 528 (1964).

C-O bending mode, respectively. These bands appear for the three tris(dithiooxalato) complexes studied here. Corresponding bands at 1600 and 1070 cm.⁻¹ were observed for [Co(en)₂(C₂S₂O₂)]Cl, but no band appeared which clearly corresponded to the coupled C-S and C-C mode.

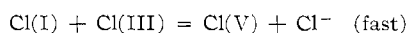
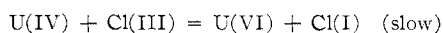
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Stoichiometry of the Reaction between Uranium(IV) and Chlorite

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Received June 8, 1964

The stoichiometry of the reaction between uranium(IV) and chlorite was studied at room temperature with rapid mixing techniques. Under some conditions, results consistent with the mechanism



and the over-all reaction



were obtained. Analyses were performed on the amount of U(IV) consumed and Cl(V) [*i.e.*, ClO₃⁻] produced in the reaction. The value of the [Cl(III)]/[U(IV)]_{consumed} ratio in the absence of scavengers was found to vary from 1.5 to 2.5. With phenol present initially, the second (fast) step was not observed and the [Cl(III)]/[U(IV)]_{consumed} ratio decreased to 1. This is used as evidence that Cl(I) is indeed an intermediate. Kinetic experiments between U(IV) and Cl(I), Cl(III), Cl(IV), and Cl(V) were carried out to obtain further evidence for the proposed mechanism. The results of these studies showed that the relative rates of the reaction between U(IV) and the various halogenates were Cl(III) > Cl(IV) > Cl(I) > Cl₂ > Cl(V).

The reaction between uranium(IV) and chlorite was studied previously by means of oxygen tracer experiments.¹ The results of these experiments were quite complex and indicated that the stoichiometry of the reaction must be better understood in order that a detailed mechanism could be proposed. This research was taken up with this purpose in mind.

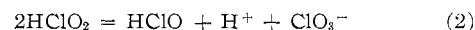
For most of the reactions of uranium(IV) reported in the literature, the stoichiometry is not complicated. However, it was somewhat complex in the present case in that chlorate was produced under strongly reducing conditions. This is probably brought about by the fact that the oxidation of uranium(IV) involves an overall loss of two electrons and the total reduction of the chlorite involves a gain of four electrons.

A study of the kinetics of the disproportionation of chlorite has been made by Barnett.² He reports the following rate law at 25°.

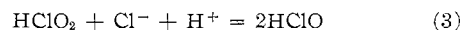
$$-d[\text{HClO}_2]/dt = 2.35 \times 10^{-2} M^{-1} \text{sec.}^{-1} \times [\text{HClO}_2]^2 \quad (1)$$

Chloride ion catalyzed the disproportionation of chlorite and changed the ratio of products formed. The fraction of the chlorite ion appearing as the product chlorate is much less in the chloride catalyzed reaction than in the uncatalyzed reaction. These observations may

be better understood by means of the mechanism proposed by Taube and Dodgen.³ In the uncatalyzed reaction, the primary step suggested is



and in the catalyzed reaction



In concentrated solutions, the oxidation of chlorite by hypochlorite is reported to yield mainly chlorine dioxide,³ which accounts for the change in the reaction products during the disproportionation of sodium chlorite.

Experimental

All of the chemicals that were used in this research were of reagent grade. Uranyl nitrate was used as the starting material in the preparation of uranyl perchlorate. The nitrate was dissolved in a solution of perchloric acid, which was in slight excess of the stoichiometric amount required to convert it to the perchlorate. The mixture was heated until it became an orange viscous mass and most of the nitrate was volatilized as nitric acid. After it was cooled, more perchloric acid was added and the above procedure was repeated until spot checks of the concentrated (>10 M) solution showed a nitrate concentration of <10⁻⁴ M. The indicator used for this was diphenylbenzidine dissolved in concentrated sulfuric acid. The resulting uranium perchlorate pentahydrate was recrystallized twice from water.⁴

It was critical for this study that the uranium solutions be free

(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.

(2) J. Barnett, Thesis, University of California, 1935.

(3) H. Taube and H. Dodgen, *J. Am. Chem. Soc.*, **71**, 3330 (1949).

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

of chloride ion. In the standard electrolytic reduction of uranium(VI) to uranium(IV), the electrolysis is carried out until the solution shows evidence of uranium(III). The uranium(III) is then converted to uranium(IV) by a stream of oxygen. However, this method has some disadvantages since the uranium(III) that is produced has been shown to reduce ClO_4^- to Cl^- .¹ Therefore, uranium(IV) was prepared by controlled potentiometric reduction of uranyl perchlorate in approximately 3 *M* HClO_4 . Careful analysis of the stock uranium(IV) solution prepared by the latter method showed the absence of chloride ion.

The uranium(IV) solutions were analyzed by a modification of the standard Ce(IV) titration.⁵ Aliquots of the uranium(IV) solutions were added to a known excess of cerium(IV) sulfate, followed by the addition of excess sodium iodide. The iodine liberated was titrated with standard thiosulfate and the uranium(IV) concentration was calculated directly. The method was reproducible to better than 1 p.p.t. (part per thousand). Chloride ion present at 1.0 or 2.0 *M*, chlorate present at 0.5 *M* (in the presence of 1 *M* chloride ion), and hydrogen ion concentrations from 0.5 to 5.0 *M* do not influence the analysis of uranium(IV) by excess cerium(IV). Another advantage of this method was that the excess cerium(IV) was used as a quenching agent for the stoichiometric experiments.

It should be pointed out that the reaction between uranium(IV) and chlorate in acid solution has been observed to be extremely slow. For example, in a solution containing 10^{-2} *M* U(IV), 10^{-2} *M* ClO_3^- , and 1 *M* HClO_4 , no reaction was observed to take place in a period of 4 hr. at 25°. Even at temperatures as high as 50°, very little if any reaction occurs in a period of 1 hr. This slow reaction between uranium(IV) and chlorate allowed for the separate analysis for each of these species in the presence of the other.

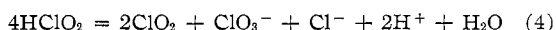
The hydrogen ion concentration of the uranium(IV) solutions was determined by means of ion-exchange techniques. Aliquots of the acidic uranium(IV) solution were passed through a column of Dowex-50 in the hydrogen ion form, and the resulting acid was titrated with standard sodium hydroxide using phenolphthalein as the indicator. Correction was made for the hydrogen ions that were released from the column by the uranium ions.

One of the products of the ClO_2^- -U(IV) reaction is ClO_3^- which was determined in the presence of Cl^- and U(IV). In the method used, Cl^- and U(IV) did not affect the results. In this procedure, a cold solution of sodium bromide was added to the chlorate sample in a glass-stoppered flask. Cold HCl was added immediately to increase the hydrogen ion concentration to 7-9 *M*. The solution was allowed to come to room temperature and to stand for about 6-8 min. The resulting solution was cooled to 0° and followed by the addition of a 1% KI solution at 0°. The iodine liberated was titrated with standard thiosulfate. With reasonable care, it was possible to attain an accuracy of better than 2 p.p.t. without any interference from U(IV) or Cl^- .

Chloride ion was also analyzed in the presence of U(IV) and ClO_3^- by means of the Volhard method by using nitrobenzene. With the use of a blank and standard chloride samples, the method was found to be completely reproducible in the presence of U(IV) and ClO_3^- .

Sodium chlorite was obtained from Matheson Coleman and Bell. Analysis of the chlorite showed >99% NaClO_2 and 0.47% NaCl . The additional impurity was presumed to be NaClO_4 .

Chlorine dioxide was prepared by acidification of NaClO_2 solutions which were allowed to disproportionate.^{2,3}



After ca. 5 hr., an aliquot of the solution was then checked for residual chlorite by removing the ClO_2 formed by extraction with CCl_4 . The remaining aqueous portion was analyzed for oxidizing species. None other than ClO_3^- was found.

The method used for the preparation of HOCl involved the production of a CCl_4 solution of Cl_2O . The Cl_2O was obtained by passing gaseous Cl_2 through a stirred suspension of yellow

mercury(II) oxide in CCl_4 . The freshly prepared solution of the Cl_2O was used immediately in the preparation of the HOCl by shaking the Cl_2O solution with water. The HOCl was stored as a slush at -20° where decomposition to form Cl^- , Cl_2 , O_2 , and ClO_3^- is slow.

Neutral solutions of sodium chlorite were always added to excess uranium(IV) solutions of the appropriate acidity. Immediately following the reaction, three aliquots were removed from the reaction vessel. The first one was discharged into excess cerium(IV) for the excess uranium(IV) analysis. The second and third aliquots were analyzed separately for chloride and chlorate.

To verify the assumption that U(IV), Cl^- , and ClO_3^- (in addition to H^+ , Na^+ , and ClO_4^-) were the only species which persist in the final solution, each reaction mixture was tested by the addition of a small aliquot to a concentrated solution of NaI to which starch was added. If any ClO_2^- , OCl^- , or Cl_2 had remained in the final reaction mixture, the iodide would have been oxidized to iodine and the purple color of the positive starch-iodine test would have been observed. A positive iodine test was observed only in the reaction with Cl^- (due to Cl_2 formed), Br^- (due to Br_2 formed), and in some of the 1.5 *M* HClO_4 solutions (due to ClO_2 formed) as noted later in this paper.

When the reaction was performed in the presence of bromide, the method of analysis was slightly different. Only the U(IV) analysis was performed, since the bromide would interfere in the Volhard titration and the bromine formed in the reaction would interfere with the chlorate analysis. The bromine formed had to be corrected for in the U(IV) analysis since bromine also can oxidize the iodide. The amount of bromine that was present was determined by addition of an aliquot of the reaction mixture to an iodide solution directly and the iodine produced was titrated with standard thiosulfate. The amount of iodine produced was then subtracted from the amount of U(IV) consumed that had been determined by means of the Ce(IV) analysis of the U(IV)- Br_2 mixture. Analysis of standard samples showed the method to be reliable to better than 3 p.p.t.

Phenol when present in the stoichiometric reactions interfered with the chlorate analysis by forming 2,4,6-tribromophenol. In the standard method of uranium analysis, the Ce(IV) solution reacted with the phenol to produce a dark purple color which completely masked the starch-iodine end point. Therefore, the U(IV) was analyzed spectrophotometrically. Standard solutions of U(IV) were used to prepare calibration curves at the various hydrogen ion concentrations used for the stoichiometric studies. The concentration of the U(IV) was obtained graphically and the results were reproducible to better than 2 p.p.t.

The experimental procedure for the kinetic studies was as follows: The uranium(IV), HClO_4 , and NaClO_2 were added to the absorption cell which was maintained at constant temperature by means of a refrigerated temperature bath which was connected directly to the cell compartment. The cell was anchored in the compartment by means of a special wooden plate to prevent movement of the cell during the rapid mixing of the reactants. The needle of a special rapid mixing syringe was carefully fitted through the opening of the compartment and into the center of the serum cap which covered the cell. When the syringe was firmly resting on the top of the cover, it was screwed securely into place. The top of the serum cap also had a short end of a needle projecting through it to relieve the pressure which built up when the solution was released from the syringe into the cell. With this apparatus, it was possible to achieve mixing times of 30 msec., as shown by Gordon and Thompson.⁸ The method of analysis used for the kinetic studies was the spectrophotometric determination of U(IV) at 6484 Å. by means of a Beckman DU spectrophotometer.

Results and Discussion

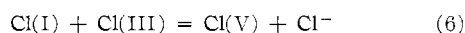
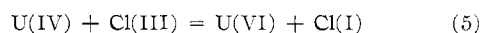
Initial work on the uranium(IV)-chlorite reaction was reported by Kern and Gordon as part of a general

(5) A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., New York, N. Y., 1953, p. 318.

(6) R. Thompson and G. Gordon, *J. Sci. Instr.*, **41**, 480 (1964).

survey on the reaction between uranium(IV) and various halogenates.¹ Table I summarizes the results of a study of the stoichiometry at various hydrogen ion concentrations.

A mechanism consistent with these results is⁷



Since the reaction between U(IV) and chlorate is slow at room temperature, ideally, this would result in the over-all reaction.



TABLE I
THE STOICHIOMETRY OF THE U(IV)-Cl(III) REACTION WITH
0.026 M [U(IV)]₀ AND 0.025 M [Cl(III)]₀ AT 25°

[H ⁺] ₀ , M	[Cl ⁻ + Cl(V)] ^a / [Cl(III)] ₀ ^e	[Cl(III)]/ [U(IV)] _{consumed}
0.16 ^b	1.04	1.50
0.19 ^c	1.06	1.64
0.40 ^c	1.00	1.89
0.60 ^d	1.01	2.05
1.00 ^d	1.00	2.13
1.50 ^d	1.00	2.13
2.00 ^d	1.00	2.14

^a Amount formed. ^b 0.0227 M [U(IV)]₀ and 0.0104 M Cl(V) formed. ^c 0.0110 M Cl(V) formed. ^d 0.0115 M Cl(V) formed. ^e This column reflects the amount of halogen products found *vs.* the amount initially present. Ideally this ratio should be 1.00. Subscript zero denotes initial concentration.

The stoichiometric coefficients of this equation indicate that the [Cl(III)]/[U(IV)]_{consumed} ratio should be 2. The [Cl(III)]/[U(IV)]_{consumed} ratio ranges from a low of 1.50 in 0.16 M HClO₄ to a high of 2.14 in 2.00 M HClO₄, and it is evident that the U(IV) is more completely consumed in solutions of lower acidity than in those of higher acidity.

In addition to reactions 5 and 6, other reactions can be proposed to account for the disappearance of U(IV) and Cl(III) and the deviations in the observed stoichiometry. These include the reaction between U(IV) and Cl(I) following eq. 5 instead of eq. 6. As will be shown later, the U(IV)-Cl(I) reaction is *much* slower than the U(IV)-Cl(III) reaction and at least an order of magnitude slower than the reaction shown by eq. 6. It might also be suggested that the Cl(III) disproportionates rapidly to form Cl(V), Cl(IV), and Cl⁻ and that Cl(IV) is the species which reacts directly with U(IV). It has been shown previously, however, that the disproportionation of Cl(III) is relatively slow.^{2,3} Therefore, when the rate of the disproportionation of Cl(III) is compared to the rate of reaction between U(IV) and Cl(III) it can be seen that the direct reac-

tion of Cl(III) to form Cl(V), Cl(IV), and Cl⁻ must play at most a minor role in the over-all reaction between U(IV) and Cl(III). In addition, the details of the reaction between U(IV) and Cl(IV) also have been studied and this reaction is considerably slower than the U(IV)-Cl(III) reaction. Finally, a direct study of the Cl(III)-Cl(I) reaction in dilute solution (under conditions similar to those obtained in the U(IV)-Cl(III) reaction) results principally in the formation of Cl(V) and not Cl(IV). The results and discussion following are presented in an attempt to substantiate the mechanism proposed in eq. 5, 6, and 7 and to show that the various side reactions described above contribute only to the deviations from the ideal stoichiometry.

A more detailed study of the stoichiometry was carried out at three specific hydrogen ion concentrations (0.18, 0.60, and 1.50 M) in an attempt to study the change of the initial [Cl(III)]/[U(IV)] ratios on the stoichiometry of reaction 7. Table II summarizes these results for 0.60 M HClO₄.

A possible explanation for the change in the [Cl(III)]/[U(IV)]_{consumed} ratio is that with the high excess of [U(IV)], the species U_{aq}⁴⁺ acts as a scavenger of Cl(I) by an association reaction. Even at these ionic strengths, an ion with a charge of +4 will be strongly associated *via* ion-pair formation. Thus increasing the concentration of excess U(IV) increases the rate of reaction 5 with respect to a process such as (4), but further increases in the concentration of U(IV) result in the removal of Cl(I), and these two tendencies oppose each other, which results in a maximum in the consumed ratio.

TABLE II
STOICHIOMETRY OF THE U(IV)-Cl(III) REACTION IN 0.60 M
HClO₄ AT 25°^a

[U(IV)] ₀ , M	[Cl(III)] ₀ , M	[Cl(III)]/ [U(IV)] _{consumed}
0.0316	0.0228	1.95
0.0262	0.0225	2.00
0.0268	0.0201	2.08
0.0277	0.0150	2.20
0.0277	0.0101	2.28
0.0258	0.00500	1.87
0.0258	0.00104	1.73
0.0158	0.0228	2.01

^a Subscript zero denotes initial concentration.

When the chlorite was initially injected into the U(IV) solution, a transient yellow color was observed. Kanyevskii and Fedorova⁸ have used this color as evidence for the production of chlorine dioxide in the reduction of chlorite by uranium(IV). Gordon and Kern⁹ have shown that the yellow color observed was not chlorine dioxide and that the transient color which appears can be interpreted in terms of the equilibrium



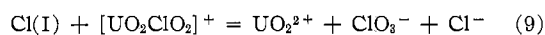
with $Q_{\epsilon 3700 \text{ \AA}} = 1 \times 10^4$, where Q is the equilibrium constant for eq. 8 and ϵ is the molar extinction coefficient for the species [UO₂ClO₂]⁺.

(8) E. Kanyevskii and L. Fedorova, *Radiokhimiya*, **3**, 339 (1961).

(9) G. Gordon and D. M. H. Kern, *Inorg. Chem.*, **3**, 1055 (1964).

(7) No attempt will be made to differentiate between HOCl and OCl⁻, although under the conditions of these experiments, in the absence of Cl⁻ the predominant chlorine(I) species is presumably HOCl. As the reaction progresses and Cl⁻ is formed, OCl⁻ and Cl⁻ rapidly react to form Cl₂. Although it is not possible to distinguish between [OCl⁻ + Cl⁻] and Cl₂ by means of these experiments, both would be consistent with the evidence presented (*vide infra*). Likewise, the other chlorine-containing species will be referred to as follows: ClO₂⁻ and HClO₂ as Cl(III), dissolved ClO₂ as Cl(IV), and ClO₃⁻ as Cl(V). In specific cases, where additional experimental evidence is available from this study with respect to the exact species involved, the formula of that halogenate has been used directly.

The formation of this charge-transfer complex could be involved in the formation of the chlorate (e.g., the Cl(I) could oxidize the $[\text{UO}_2\text{ClO}_2]^+$).



Therefore, a series of experiments was performed in the presence of excess UO_2^{2+} to ascertain whether or not this species could be a contributing factor to the mechanism.

If the $[\text{UO}_2\text{ClO}_2]^+$ complex were involved in the formation of ClO_3^- , the $[\text{Cl(III)}]/[\text{U(IV)}]$ ratio should increase in experiments with excess UO_2^{2+} . From the results shown in Table III, it appears that the addition of UO_2^{2+} does not affect the stoichiometry and that the complex does not play an important role in the reaction.

TABLE III

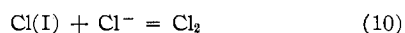
THE EFFECT OF URANYL ION ON THE STOICHIOMETRY OF THE U(IV)-Cl(III) REACTION IN 0.60 M HClO_4 AT 25°

$[\text{UO}_2^{2+}]_0$, M	$[\text{Cl(III)}]/[\text{U(IV)}]_{\text{consumed}}$
0.000 ^a	2.04
0.015 ^a	2.03
0.030 ^a	2.03
0.054 ^a	2.04
0.000 ^b	1.73
0.020 ^b	1.72
0.030 ^b	1.73

^a With 0.0277 M $[\text{U(IV)}]_0$ and 0.0230 M $[\text{Cl(III)}]_0$. ^b With 0.0258 M $[\text{U(IV)}]_0$ and 0.00104 M $[\text{Cl(III)}]_0$. Subscript zero denotes initial concentration.

If the Cl(I) intermediate were removed before it could react with either the U(IV) or the Cl(III), the $[\text{Cl(III)}]/[\text{U(IV)}]$ ratio should decrease to a minimum of 1.0. Experiments were performed using Cl^- , Br^- , and phenol as scavengers for Cl(I).

Chloride is known to react rapidly with Cl(I) to form dissolved chlorine¹⁰



which has been shown to oxidize uranium(IV) only slowly.¹ Table IV summarizes the results of the reaction in the presence of added Cl^- .

TABLE IV

THE EFFECT OF Cl^- ON THE STOICHIOMETRY OF THE U(IV)-Cl(III) REACTION WITH 0.0275 M $[\text{U(IV)}]_0$ AND 0.0226 M $[\text{Cl(III)}]_0$ IN 0.60 M HClO_4 AT 25°^a

$[\text{Cl}^-]_0$, M	$[\text{Cl(III)}]/[\text{U(IV)}]_{\text{consumed}}$
0.000	1.96
0.027	1.87
0.054	1.82

^a Subscript zero denotes initial concentration.

From these results it appears that the effect of chloride ion on the stoichiometry is minor. However, these results are surprising since it is expected that chlorine produced will oxidize the chlorite to form chlorate. Chlorine can also react as an intermediate with chlorite in the same manner as the hypochlorite. Some recent work that has been done in this laboratory has shown

that in dilute solution chlorine oxidizes chlorite even more rapidly than hypochlorite to produce chlorate as the principal product.¹¹ Therefore, it was necessary to find a better scavenger for the proposed Cl(I) intermediate.

Bromide ion appeared to be better than chloride ion since the reaction between Cl(I) and Br^- to form Br_2 is rapid and Br_2 only slowly oxidizes U(IV).¹² Experiments were performed in the presence of Br^- ion and the results are shown in Table V.

TABLE V

THE EFFECT OF Br^- ON THE STOICHIOMETRY OF THE U(IV)-Cl(III) REACTION WITH 0.0268 M $[\text{U(IV)}]_0$ AND 0.0226 M $[\text{Cl(III)}]_0$ IN 0.60 M HClO_4 AT 25°

$[\text{Br}^-]_0$, M	$[\text{Cl(III)}]/[\text{U(IV)}]_{\text{consumed}}$
0.000	1.99
0.013	1.33
0.026	1.29
0.052	1.19
1.000	1.49
2.000 ^a	2.22

^a With 0.0279 M $[\text{U(IV)}]_0$ and 0.0225 M $[\text{Cl(III)}]_0$. Subscript zero denotes initial concentration.

Although at low concentrations Br^- ion appears to be a much better scavenger for Cl(I) than was Cl^- ion, it should be pointed out that the results are affected by the oxidation of the excess U(IV) by the Br_2 produced. It is also observed that when the initial concentration of Br^- ion is greatly increased the ClO_2^- preferentially reacts with the Br^- . Another set of experiments was carried out at 0° in the presence of Br^- ion to minimize the oxidation of the U(IV) by Br_2 . These results are summarized in Table VI.

Although the U(IV)- Br_2 reaction is minimized, the side reaction of Br_2 with Cl(III) appears to affect the results markedly. A better scavenger was still needed.

TABLE VI

THE EFFECT OF Br^- ON THE STOICHIOMETRY OF URANIUM(IV)-CHLORITE WITH 0.0281 M $[\text{U(IV)}]_0$ AND 0.0227 M $[\text{Cl(III)}]_0$ IN 0.60 M HClO_4 AT 0°^a

$[\text{Br}^-]_0$, M	$[\text{Cl(III)}]/[\text{U(IV)}]_{\text{consumed}}$
0.000	1.96
0.026	1.57
0.052	1.26
1.000	1.75

^a Subscript zero denotes initial concentration.

Phenol is known to react with Cl(I) to form an addition compound.¹³ Therefore, phenol was next used as a scavenger to try to remove the proposed Cl(I) intermediate. In preliminary experiments, it was found that the spectrum of a U(IV) solution was not changed in the presence of phenol. It was also shown that Cl(III) did not react independently with phenol, in the following way. Some phenol was added to an

(11) F. P. Emmenegger and G. Gordon, unpublished results (1964).

(12) G. Gordon and A. Andrewes, *Inorg. Chem.*, **3**, 1733 (1964).

(13) P. B. D. De La Mare, A. D. Ketley, and C. A. Vernon, *J. Chem. Soc.*, 1290 (1954).

aqueous solution of sodium chlorite which was allowed to stand for several minutes. The phenol was then extracted with benzene and carbon tetrachloride, and the Cl(III) remaining was analyzed in the usual manner. The results showed that there was no detectable reaction between Cl(III) and the phenol, in minutes, in the absence of U(IV).

The results of the reactions performed between U(IV) and Cl(III) in the presence of phenol are summarized in Table VII.

TABLE VII

THE EFFECT OF PHENOL ON THE STOICHIOMETRY OF THE URANIUM(IV)-CHLORITE REACTION WITH 0.0277 M [U(IV)]₀ AND 0.0226 M [Cl(III)]₀ IN 0.60 M HClO₄ AT 25°^a

[phenol] ₀ , M	[Cl(III)]/[U(IV)] _{consumed}
0.000	1.99
0.013	1.01
0.027	1.02
0.054	1.01

^a Subscript zero denotes initial concentration.

If all the Cl(I) were quantitatively removed, the [Cl(III)]/[U(IV)] ratio should decrease to 1.00. Therefore, from the results shown in Table VII, phenol appears to be an excellent scavenger for the proposed Cl(I) intermediate.

The difference in the shape of the second-order reaction curves with and without phenol for the reaction between uranium(IV) and chlorite was quite marked. In the presence of phenol the reaction between U(IV) and Cl(III) is first order with respect to both U(IV) and Cl(III). The rate of the U(IV)-Cl(III) reaction in the absence of phenol decreases markedly after approximately 70% of the reaction is over. This decrease does not occur in the presence of phenol, and a graph of log [Cl(III)]/[U(IV)] as a function of time is linear for more than four half-lives. The change in slope in the absence of phenol is presumably caused by the Cl(III) reacting by another path [*e.g.*, with Cl(I) to form Cl(V) and Cl⁻, thus leaving less to react with the U(IV)]. In the reaction with phenol present, the Cl(I) is rapidly removed and Cl(I) is not available for this second reaction.

Another set of experiments was performed to show that phenol also retards the oxidation of U(IV) by Cl(I) for additional evidence that Cl(I) is indeed the intermediate which is being removed. These results are given in Table VIII. Under these conditions, the phenol efficiently removes the Cl(I) and prevents it from oxidizing the U(IV).

Various other experiments on the stoichiometry of

TABLE VIII

THE U(IV)-Cl(I) REACTION WITH 0.0364 M [U(IV)]₀ AND 0.0339 M [Cl(I)]₀ IN 1 M HClO₄^a

Reactants	Fraction of reaction completed		
	1 min.	3 min.	6 min.
U(IV) + Cl(I)	0.120	0.837	0.980
U(IV) + Cl(I) + phenol	0.000	0.014	0.036

^a Subscript zero denotes initial concentration.

the U(IV)-Cl(III) reaction were also carried out in 0.18 and 1.50 M HClO₄. These results are summarized in Tables IX and X.

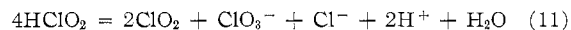
As the hydrogen ion concentration increases, the [Cl(III)]/[U(IV)] ratio also increases. This is probably due to the fact that the rate of disproportionation of ClO₂⁻, although relatively low compared to the rate of the U(IV)-Cl(III) reaction, is directly proportional to the square of the hydrogen ion concentration and results in the production of some ClO₂ in the 1.5 M HClO₄ solutions as shown in eq. 11.

TABLE IX

STOICHIOMETRY OF THE U(IV)-Cl(III) REACTION IN 0.18 M HClO₄

Added species	[Cl(III)]/[U(IV)] _{consumed}
None ^a	1.67
None ^b	1.76
None ^c	1.89
None ^d	1.54
0.027 M Cl ^{-e}	1.68
0.054 M Cl ^{-e}	1.69
0.013 M Br ^{-e}	1.34
0.054 M Br ^{-e}	1.15
0.027 M phenol ^e	1.01
0.054 M phenol ^e	1.01

^a 0.0281 M [U(IV)]₀ and 0.0226 M [Cl(III)]₀. ^b 0.0272 M [U(IV)]₀ and 0.0148 M [Cl(III)]₀. ^c 0.0272 M [U(IV)]₀ and 0.0100 M [Cl(III)]₀. ^d 0.0272 M [U(IV)]₀ and 0.00522 M [Cl(III)]₀. ^e 0.0277 M [U(IV)]₀ and 0.0226 M [Cl(III)]₀. Subscript zero denotes initial concentration.



In 1.5 M HClO₄ solution after several minutes (more than sufficient time for completion of the U(IV)-Cl(III) reaction), the solution showed a positive I₂ test. Cl(V) does not react with I⁻ under these conditions, and this is in contrast to the negative I₂ tests observed in solutions of lower acidity. The oxidizing species that persists in the solution was shown to be ClO₂. Therefore, the [Cl(III)]/[U(IV)]_{consumed} ratio shown in Table X directly reflects the formation of the Cl(IV) from Cl(III) in addition to the U(IV) and Cl(III) consumed by the direct U(IV)-Cl(III) reactions. The results in 1.5 M HClO₄ are further complicated by the fact that the U(IV) and the Cl(IV) formed do react at a slower but finite rate. The proposed mechanism is strongly supported by the results in 1.5 M HClO₄ by the

TABLE X

STOICHIOMETRY OF THE U(IV)-Cl(III) REACTION WITH 0.0277 M [U(IV)]₀ IN 1.5 M HClO₄

[Cl(III)] ₀ , M	Added species	[Cl(III)]/[U(IV)] _{consumed}
0.0226	None ^a	2.15
0.0150	None	2.30
0.00997	None	2.51
0.00496	None	1.90
0.0226	0.054 M Cl ⁻	2.00
0.0226	0.013 M Br ⁻	1.48
0.0226	0.054 M Br ⁻	1.33
0.0100	0.027 M phenol	1.03
0.0101	0.054 M phenol	1.02

^a 0.0280 M [U(IV)]₀. Subscript zero denotes initial concentration.

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* HClO₄.

It is also interesting to note that the maximum in the $[Cl(III)]/[U(IV)]_{\text{consumed}}$ 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 ClO₂⁻ oxidizes U(IV) more rapidly than Cl₂, OCl⁻, or ClO₂. In order for the ClO₂ to play a major role, it would have to be produced and oxidize the U(IV) much more rapidly than does the ClO₂⁻. 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 ClO₂, ClO₂⁻, 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.

Uranium(IV) was most rapidly oxidized by ClO₂⁻ under all conditions. The relative rates of reactions

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

[U(IV)], <i>M</i>	Halogen	[H ⁺], <i>M</i>	Temp., °C.	<i>k</i> , ^a <i>M</i> ⁻¹ sec. ⁻¹
0.0387	0.0297 <i>M</i> Cl(III)	0.25	0	4.6
0.0194	0.0297 <i>M</i> Cl(III)	0.25	0	4.0
0.0387	0.0297 <i>M</i> Cl(III)	0.25	25	22
0.0387	0.0297 <i>M</i> Cl(III)	1.30	25	18
0.0387	0.0323 <i>M</i> Cl(IV)	0.25	25	6.5
0.0304	0.0339 <i>M</i> Cl(I)	0.25	25	4.1

^a Apparent second-order rate constant.

between U(IV) and various halogenates were ClO₂⁻ > ClO₂ > OCl⁻ > Cl₂ > ClO₃⁻.

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 ClO₂⁻ and U⁴⁺ or HClO₂ and UOH³⁺. 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.

Acknowledgments.—The authors wish to express their gratitude to the National Science Foundation for financial support of this research.

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The Oxidation of Aqueous Uranium(IV) by Bromine

BY GILBERT GORDON AND ARTHUR ANDREWES

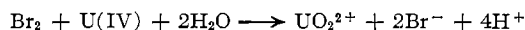
Received June 10, 1964

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 Kern¹ 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 UO₂²⁺ and the reduction of Br₂ to 2Br⁻. It is apparent from the stoichiometry of the reaction



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

(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.