this behavior but rather that the similarities in the chemistry of Ce(III) and Am(III) are realized in this investigation of synergism. Ke and Li[4] investigated the Co(II) and Zn(II) systems but unfortunately the only species they investigated were R_3N and R_3NHT. A comparison with our work cannot be made since we excluded R_3N as a species. However, it is interesting to note how difficult it was for Ke and Li to quantitate the differences in complexing ability between R_3N and R_3NHT. Namely, they had to utilize trends in the values of K_s, (5.6–6.3) $\times 10^5$ in the case of cobalt and (3.3–4.3) $\times 10^4$ in the case of zinc.

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The Kinetics and Mechanism of the Oxidation–Reduction Reaction between Uranium(IV) and Chlorine(III) in the Presence of Phenol in Aqueous Acid Solution

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The oxidation–reduction reaction between uranium(IV) and chlorine(III) was studied in the presence of 0.1 *M* phenol. The addition of phenol to the reaction mixture effectively removes the side reactions of the chlorine-containing intermediates. Under these conditions the stoichiometry of the reaction becomes U(IV) + Cl(III) + phenol → U(VI) + H^+ + chlorophenols. The results of an oxygen-18 tracer experiment suggest that the principal pathway involves a two-electron oxygen atom transfer from the oxidant to the reductant. An increase in the concentrations of both chlorine(III) and hydrogen ion retards the rate of the reaction. The data are consistent with the rate expression $-d[U(IV)]/dt = k_1[U(IV)][Cl(III)]/\{1 + K_2[HClO_2]\}\{1 + K_3[H^+]\}$. At 25°, $k_1 = 291.3 \pm 4.2\ M^{-1}\ sec^{-1}$, $K_2 = 4.13 \pm 0.25\ M^{-1}$, and $K_3 = 20.8 \pm 3.2\ M^{-1}$. Mechanistically, the rate law is interpreted in terms of a hydrogen ion dependent two-electron transfer reaction and the formation of a nonproductive intermediate.

Introduction

Oxidation–reduction reactions of a variety of metal ions and chlorine oxidants[1–18] have been the subject of many studies in recent years. Of particular interest in these studies has been the mechanism by which these reactions occur. A fundamental objective is to determine if these processes occur by direct transfer of one or two electrons or by atom or group transfer. A secondary objective is the distinction between an inner-sphere and an outer-sphere process. A detailed knowledge of the reaction stoichiometry, the composition and geometry of the reactants, the activated complex, and the products is essential for the successful interpretation of the mechanism.

The present study was initiated in an attempt to understand better those factors which influence reactivity patterns of the chlorine oxidants with metal ions. In this study the oxidation of uranium(IV) by chlorine(III) affords the possibility of either two successive one-electron transfers or one two-electron transfer to produce uranium(VI). Another property of uranium is that uranium(IV) exists in aqueous solution as the hydrated U_{aq}^{4+} ion and uranium(VI) exists as the oxy cation UO_2^{2+}. Presumably the water molecules in the first coordination sphere of uranium(IV) are labile, whereas the oxygens of uranium(VI) are known to exchange with solvent water oxygen very slowly.[19,20] Since the oxygens of chlorine(III) are inert to substitution[21] in aqueous solution, all of the prerequisites for a possible meaningful tracer study are fulfilled.

The reaction of uranium(IV) and chlorine(III) was previously studied by Gordon and Kern[16] as part of a general survey of halogenate oxidations of uranium(IV). In this preliminary work, the reaction was found to be quite complex owing to a change in stoichiometry during the course of the reaction. In an attempt to understand better this reaction Gordon and Feldman[22] studied the detailed stoichiometry. They observed, depending on initial reaction conditions, that the stoichiometry of the reaction varied from 1.5 to 2.5 chlorine(III) consumed per uranium(IV). From their observations, they postulated the mechanistic scheme

$$\mathrm{U(IV)} + \mathrm{Cl(III)} \longrightarrow \mathrm{U(VI)} + \mathrm{Cl(I)} \qquad \text{slow} \qquad (1)$$

$$x\mathrm{Cl(III)} + \mathrm{Cl(I)} \longrightarrow y\mathrm{Cl(V)} + z\mathrm{Cl}^- \qquad \text{fast} \qquad (2)$$

to give

$$\mathrm{U(IV)} + (1 + x)\mathrm{Cl(III)} \longrightarrow \mathrm{U(VI)} + y\mathrm{Cl(V)} + z\mathrm{Cl}^- \qquad (3)$$

as the overall stoichiometry. Reaction 1 is rate deter-

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mining, since from an independent study[23] reaction 2 is known to have a rate more than 40 times greater than reaction 1. Reaction 2 is also proposed to account for the production of chlorate ion as a product.

Experimental Section

Uranium(IV) perchlorate was prepared by the controlled electrolytic reduction of uranium(VI) perchlorate.[16] Provided the solution was kept cold, the reaction went to completion with no formation of uranium(III) or chloride ion. The concentration of uranium(IV) was determined by titrating an aliquot of the stock solution with ceric sulfate at 50° using ferroin as the indicator.

The hydrogen ion concentration in the uranium stock solution was determined by passing an aliquot of solution through a cation-exchange column containing Dowex 50W-X12 resin. The effluent was titrated with standard sodium hydroxide to a phenolphthalein end point. The actual hydrogen ion concentration was calculated as

$$[H^+]_{analytical} = [H^+]_{titrated} - 4[U(IV)] - 2[U(VI)]$$

Sodium chlorite was obtained from Matheson Coleman and Bell and analyzed for impurities by standard analytical techniques.[24-26] Analysis of the solid showed 98.8% sodium chlorite, 0.23% sodium hypochlorite, 0.26% sodium chloride, and 0.79% sodium chlorate. In each kinetic experiment the concentrations of freshly prepared sodium chlorite solutions were determined by standard iodometric techniques.

The ionic strength of each experiment was maintained at 2.00 ± 0.05 M by adding appropriate amounts of sodium perchlorate. Stock solutions of sodium perchlorate were prepared by neutralizing reagent grade sodium carbonate with perchloric acid.[1] The salt was recrystallized three times from distilled water to ensure purity. The sodium perchlorate was standardized by passing an aliquot of the stock solution through a Dowex 50W-X12 cation-exchange resin and by titrating the effluent with standard sodium hydroxide.

Phenol, crystalline and liquefied, was obtained from Mallinckrodt Chemical and used without further purification. The liquefied phenol is a solution which is 88% phenol and 12% water by weight. The phenol stock solutions were prepared either by weighing the solid or by taking a volume of liquefied material and diluting to 100 ml in a volumetric flask. The final concentrations were determined spectrophotometrically at 270 nm where the molar absorptivity[27] is 1450 M^{-1} cm^{-1}. The results of the kinetic runs with crystalline and liquid phenol were the same; thus, because of the ease of handling of the crystalline material, it was used throughout this study.

The rate at which uranium(IV) reacts with chlorine(III) was followed by observing the decrease in absorbance as a function of time on a Cary 14R spectrophotometer. The wavelength chosen for this study was 648 nm. At this wavelength uranium(IV) exhibits a maximum with a molar absorptivity[28] of 60.0 M^{-1} cm^{-1}, and under the conditions of the kinetic experiments, the other species in solution have negligible absorbances. The reaction was not monitored in the ultraviolet region because of overlapping spectra of the reactants and the products.

In a typical kinetic run, a volume of the uranium(IV) solution was delivered into a 2-cm cylindrical quartz cell by means of a calibrated syringe.[29] The cell was fitted with a serum cap and placed in the thermostated cell compartment of a Cary 14R spectrophotometer and allowed to come to temperature equilibrium. A spring-powered syringe,[30] calibrated to deliver a known volume, was filled with sodium chlorite solution. The syringe was secured in position in the spectrophotometer such that the hypodermic needle was inserted into the quartz cell through the serum cap. With the recorder moving, the reaction was initiated by triggering the spring-powered syringe and the course of the reaction was monitored spectrophotometrically.

A Durrum stopped-flow apparatus was employed to study the kinetics of the uranium(IV)–chlorine(III) reaction under pseudo-first-order conditions with chlorine(III) in excess. The experimental procedures of the stopped-flow method have been adequately described elsewhere.[31,32] Once again, 648 nm was selected as the wavelength to follow the progress of the reaction. The increase in transmittance, as the reaction proceeded, was monitored as a function of time on a Tektronix 564 storage oscilloscope. A Polaroid camera was used to photograph the oscillogram. Pseudo-first-order rate constants were determined under conditions where chlorine(III) was in at least a tenfold excess. The apparent second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the average concentration of chlorine(III) in each kinetic experiment.

The oxygen-18 tracer study was undertaken in an attempt to determine if atom transfer was involved in the uranium(IV)–chlorine(III) redox process. In a typical experiment, the volume of uranium(IV) needed to give a final concentration of 0.214 M was added to a 10-ml volumetric flask. The appropriate amounts of perchloric acid and sodium perchlorate were added such that the acidity and ionic strength were 1.00 and 2.00 M, respectively. A volume of phenol was added and the solution was diluted to the mark with 1.78 atom % oxygen-18-enriched water.

Approximately 1 ml of the freshly prepared uranium(IV) solution was transferred to a Urey tube and placed on a vacuum line. The contents of the tube were frozen with liquid nitrogen and the system was evacuated. After evacuating the system, the contents of the Urey tube were permitted to thaw. This allowed for the removal of any dissolved gas in the solution. The solution was then frozen with liquid nitrogen and further evacuated. This procedure was repeated several times. In order to determine the oxygen-18 enrichment of the reaction solution, approximately 0.5 ml of the water was distilled, under vacuum, into another Urey tube. One centimeter of normal CO_2 was bled into the tube containing the enriched water and allowed to equilibrate for 5 days in order to ensure complete exchange.[33]

In order to determine if atom transfer from chlorine(III) to uranium(IV) occurs, 5 ml of the oxygen-18-enriched uranium(IV) solution was placed in an erlenmeyer flask and submerged in an ice bath. From a calibrated syringe, 0.59 ml of sodium chlorite solution was injected into the uranium(IV) solution. The contents of the flask were thoroughly mixed and allowed to react for about 30 sec. At this time the partially reacted solution was poured through a Dowex 50W-X8 ion-exchange column. The uranium(VI) product was separated from the uranium(IV) and removed from the column by the addition of successive 5-ml aliquots of cold 1 M perchloric acid.

The procedure adopted for the precipitation of the uranyl ion was developed by Gordon and Thompson.[34] In this method cesium chloride was added until cesium perchlorate no longer precipitated from the solution. The cesium perchlorate was removed by collecting the precipitate on a medium-porosity sintered-glass filter. An additional 0.8 times the stoichiometric weight of cesium chloride was added to the filtrate. The solution was cooled in an ice bath and hydrogen chloride gas was bubbled through the solution until $Cs_2UO_2Cl_4$ just began to precipitate. The yellow crystals were collected on a filter and washed repeatedly with acetonitrile to remove as much water as possible. The salt was placed in a desiccator containing Anhydrone and evacuated for 3 days to remove the last traces of water. In order to determine the purity of the salt and ascertain that all of the water had been removed, uranium and chloride analyses were carried out. *Anal.* Calcd for $Cs_2UO_2Cl_4$: U, 35.1; Cl, 20.9. Found: U, 35.2; Cl, 20.8.

The isotopic composition of the oxygen in the uranyl salt was established by mass spectrometric analysis. In this method[35] a sample which contained about 0.1 mmol of oxygen was added to 0.1–0.2 mmol of vacuum-dried silver cyanide in a 5-ml Pyrex glass U tube which had a break-off tip and a seal-off constriction. After evacuation to less than 10^{-4} Torr, the tube was sealed and heated for 2 hr at 500° in a thermostated furnace. After cooling

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to room temperature, the tube was placed on a vacuum line and cooled to around −110° in a liquid nitrogen–methylcyclohexane slush. The break-seal of the U tube was broken by means of a magnet and the liquid nitrogen condensable gases were transferred to a Urey tube for a period of 10–15 min. Prior to warming the sample to room temperature for analysis, the noncondensable gases were removed. The isotopic composition of the purified carbon dioxide was determined by measuring the ratio of the mass 46 to the (mass 44 + mass 45) peaks by means of a Nuclide Corp. RMS-11 isotope mass spectrometer. The ratio was read directly by the double collector procedure. The enrichment of the compound was calculated from the measured ratio for the enriched and normal samples.[36]

Results

A. Effect of Phenol on the Stoichiometry and Observed Second-Order Rate Constants.—In view of the complex stoichiometry, a detailed kinetic study was initiated and a means was sought to remove the potential chlorine(I) intermediate. Of the several scavengers tested,[22] phenol was found to remove effectively the reactive intermediate chlorine species. In the absence of phenol the stoichiometry of the reaction, represented by the ratio $[\mathrm{Cl(III)}]_0/[\mathrm{U(IV)}]_{\mathrm{consumed}}$, varies between 2.01 and 2.10 depending upon the initial reactant concentrations. With the addition of phenol, the stoichiometry of the reaction decreases to a constant value of 1.00 ± 0.01.

In order to account for this change in stoichiometry with the addition of phenol, it is necessary to examine the various possible intermediate reactions. Chlorine(I) is produced according to reaction 4. The interaction of chlorine(I) with chlorine(III) is fast[23] enough such that the reaction of chlorine(I) with phenol[37] cannot account for the scavenging effects noted with phenol. The reaction between phenol and the scavenged chlorine species must be competitive with the chlorine(I)–chlorine(III) reaction and much faster than the uranium(IV)–chlorine(III) reaction. Emmenegger and Gordon[23] reported that the interaction of chlorine(I) with chlorine(III) to produce the Cl_2O_2 intermediate is rapid. The chlorination of phenol by Cl_2O_2 has also been reported to be a fast process.[27,38] In addition to the rapid interaction of Cl_2O_2 with phenol, a necessary criterion is that chlorine(III) must be regenerated to account for a decrease in stoichiometry from 2:1 to 1:1. Therefore the following mechanism, based on the stoichiometric results, is consistent with these arguments

$$\mathrm{U(IV)} + \mathrm{Cl(III)} \longrightarrow \mathrm{U(VI)} + \mathrm{Cl(I)} \quad \text{slow} \qquad (4)$$

$$\mathrm{Cl(I)} + \mathrm{Cl(III)} \longrightarrow \mathrm{Cl_2O_2} \quad \text{fast} \qquad (5)$$

$$\mathrm{Cl_2O_2} + \mathrm{C_6H_5OH} \longrightarrow \mathrm{ClC_6H_4OH} + \mathrm{H^+} + \mathrm{Cl(III)} \quad \text{fast} \qquad (6)$$

The overall stoichiometry would be

$$\mathrm{U(IV)} + \mathrm{Cl(III)} + \mathrm{C_6H_5OH} \longrightarrow \mathrm{U(VI)} + \mathrm{ClC_6H_4OH} + \mathrm{H^+} \qquad (7)$$

The chloro-substituted phenol products, which result from the uranium(IV)–chlorine(III) reaction in the presence of phenol, have been determined in this laboratory.[27] The results of this study indicate that that total amounts of *o*- and *p*-chlorophenols found account for the amount of chlorine(I) or, actually, Cl_2O_2, theoretically produced in the reaction. This is not unreasonable since Cl_2 and Cl_2O_2 react at comparable rates with phenol.[27,38]

B. The Order of the Reaction with Respect to Uranium(IV) and Chlorine(III).—In this study, the oxidation of uranium(IV) by chlorine(III) was carried out with an excess of phenol in order to ensure the complete removal of the reactive chlorine intermediate. Under conditions where phenol is in excess, the overall stoichiometry of the reaction is described by eq 7. A series of experiments was carried out to determine the order of the reaction with respect to uranium(IV) and chlorine(III) in the presence of excess phenol. These results are summarized in Table I. The data confirm earlier reports[16,22] that the reaction is first order

TABLE I

OBSERVED SECOND-ORDER RATE CONSTANTS FOR THE REACTION BETWEEN URANIUM(IV) AND CHLORINE(III) IN THE PRESENCE OF 0.1 M PHENOL AT 2.00 M IONIC STRENGTH AND 25°

10^2 [U(IV)], M	10^2 [Cl(III)], M	$[H^+]_0$, M	$[H^+]_{calcd}$,[e] M	k_{obsd}, M^{-1} sec^{-1}	k_{calcd}, M^{-1} sec^{-1}
			25.0°		
0.621	0.548	1.25	1.245	10.48 ± 0.02[a]	10.59
0.715	0.547	1.00	0.995	13.02 ± 0.06	13.13
0.726	0.588	1.50	1.494	8.90 ± 0.10	8.86
0.714	0.586	0.75	0.744	17.90 ± 0.30	17.26
0.668	1.471	0.75	0.736	16.65 ± 0.60	16.88
0.681	0.400	0.75	0.746	17.93 ± 0.30	17.35
0.668	0.714	0.75	0.743	16.45 ± 0.30	17.20
0.627	0.346	1.00	0.997	13.61 ± 0.25[b]	13.21
0.600	0.340	1.00	0.997	13.80 ± 0.12[c]	13.21
0.685	0.230	1.00	0.998	13.38 ± 0.22	13.26
0.685	0.420	1.00	0.996	12.98 ± 0.10	13.18
0.685	1.134	1.00	0.990	12.59 ± 0.13	12.91
0.657	0.806	1.00	0.992	13.20 ± 0.10	13.04
0.681	0.350	1.00	0.997	13.20 ± 0.25	13.21
0.720	13.70	1.00	0.850	11.22 ± 0.20	10.14
0.720	13.70	0.50	0.359	24.40 ± 0.10	22.92
0.700	20.00	1.00	0.811	9.23 ± 0.30	9.15
0.430	12.00	1.10	0.986	9.28 ± 0.20	9.19
0.430	10.00	1.10	1.004	9.64 ± 0.30	9.53
0.430	10.00	0.15	0.086	83.50 ± 1.00	82.60
0.430	10.00	0.50	0.410	20.20 ± 0.20	22.27
0.430	10.00	0.60	0.509	17.70 ± 0.10	18.24
0.430	10.00	0.80	0.706	12.50 ± 0.31	13.37
0.430	10.00	0.21	0.136	58.50 ± 1.50	58.21
0.430	10.00	1.10	1.005	9.50 ± 0.30[d]	9.53
			20.0°		
0.720	0.420	0.85	0.846	8.78 ± 0.01	8.48
0.710	0.417	0.75	0.746	9.64 ± 0.13	9.54
0.720	0.415	1.00	0.996	7.38 ± 0.17	7.27
0.700	10.00	1.05	0.956	5.64 ± 0.05	6.00
0.700	20.00	1.05	0.862	5.50 ± 0.05	5.46
			15.0°		
0.750	0.420	0.85	0.846	4.37 ± 0.01	4.49
0.742	0.400	0.75	0.746	4.95 ± 0.02	5.04
0.747	0.434	1.00	0.996	3.68 ± 0.01	3.87
0.700	10.00	1.05	0.956	3.51 ± 0.01	3.45
0.700	20.00	1.05	0.864	3.08 ± 0.03	3.33
			10.0°		
0.750	0.424	0.85	0.846	2.46 ± 0.01	2.31
0.744	0.400	0.75	0.746	2.74 ± 0.01	2.59
0.765	0.430	1.00	0.996	1.98 ± 0.09	1.98
0.700	10.00	1.05	0.957	2.05 ± 0.01	1.89
0.700	20.00	1.05	0.868	1.87 ± 0.02	1.92

[a] The error estimates are average deviations from the mean for replicate experiments. [b] Platinium needle used with spring-powered syringe. [c] Second-order experimental conditions for reaction carried out on the Durrum-Gibson stopped-flow spectrometer. [d] 0.50 M phenol. [e] The values of $[H^+]_{calcd}$, at various temperatures, were computed by employing the corresponding values of K_3 listed in Table II.

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with respect to uranium(IV) and chlorine(III). In the concentration range of 0.0035–0.0072 *M* uranium(IV) and 0.002–0.200 *M* chlorine(III), the data from individual kinetic experiments fit the general second-order rate equation for more than 3 half-lives of the reaction.

The fact that the observed rate constants differ for runs with different initial reactant concentrations is an indication that the reaction is more complicated than simple second order. A comparison of the results at 1.00 *M* hydrogen ion suggests that at high chlorine(III) concentrations the reaction is inhibited by chlorine(III).

C. The Effect of Hydrogen Ion on the Rate of Reaction.—The results of a series of experiments in which the hydrogen ion concentration was varied from 0.15 to 1.50 *M* are also shown in Table I. It is apparent that the observed second-order rate constant is decreased by an increase in hydrogen ion concentration.

Generally, the slope of a plot of the logarithm of the observed second-order rate constant as a function of the logarithm of the hydrogen ion concentration will indicate the order of the reaction with respect to hydrogen ion concentration. In the present system, before such a plot can be meaningful, it is necessary to account for the decrease in hydrogen ion concentration caused by the rapid equilibrium reaction

$$H^+ + ClO_2^- \overset{K_3}{\rightleftharpoons} HClO_2 \qquad (8)$$

Since chlorine(III) is introduced into the reaction as $NaClO_2$, the actual hydrogen ion concentration will depend not only on the amount of chlorite ion added but also on the magnitude of K_3.

A value of K_3 of 91 M^{-1} has been reported[39a] at zero ionic strength and 25°. More recently Hong[39b] reported a value of 40.8 M^{-1} for the association constant of chlorous acid at 1.00 *M* ionic strength and 25°. If the data of Hong are extrapolated to 2.00 *M* ionic strength, an approximate value for K_3 of 33.0 M^{-1} is obtained. As a first approximation, this value was employed to calculate the hydrogen ion concentration for each reaction mixture.

It is apparent that the correction of the hydrogen ion concentration at low chlorine(III) concentrations and the lowest hydrogen ion concentration will be only about 1%. However, at the highest chlorine(III) concentration and the low hydrogen ion concentrations, the correction is substantial. A log–log plot of the observed second-order rate constant from Table I as a function of calculated hydrogen ion concentration is shown in Figure 1. The noncoincidence of the curves at low and high chlorine(III) concentrations reflects the additional inhibition by chlorine(III).

The log–log plot at low chlorine(III) concentrations suggests that in the hydrogen ion concentration range of 0.75–1.50 *M*, the reaction is inverse first order with respect to the hydrogen ion concentration. Under conditions of high but constant chlorine(III) concentrations and in the hydrogen ion concentration range of 0.08–1.00 *M*, the reaction is less than inverse first order with respect to hydrogen ion concentrations. The implication of this observation is that at high hydrogen ion concentrations, the reaction is inverse first order with respect to hydrogen and at low hydrogen ion concentrations, the reaction tends toward a lower order. Results of this nature are indicative of consecutive reactions which are consistent with rate expressions of the type

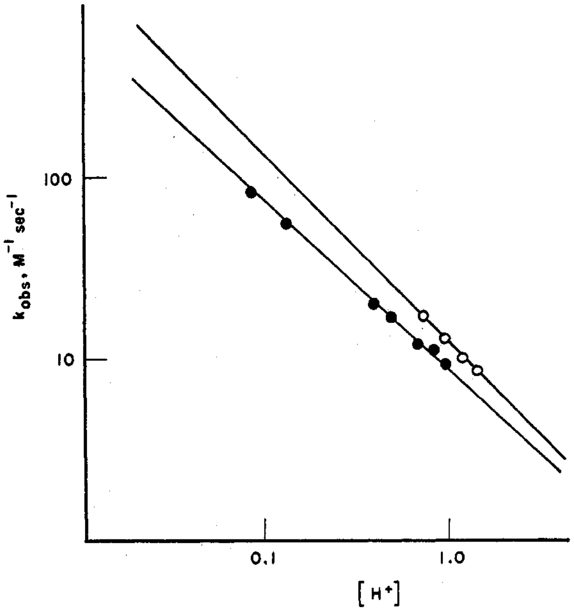

Figure 1.—The effect of hydrogen ion concentration on the rate of the uranium(IV)–chlorine(III) reaction: ○, low Cl(III) concentration, slope −1.02 ± 0.03; ●, high Cl(III) concentration, slope −0.89 ± 0.02.

$$\frac{-d[U(IV)]}{dt} = k_{obsd}[U(IV)][Cl(III)] = \frac{k_1'[U(IV)][Cl(III)]}{1 + K_3[H^+]} \qquad (9)$$

Thus by choosing an appropriate value of K_3, it follows that at low hydrogen ion concentration the observed hydrogen ion dependence will be less than inverse first order. At high hydrogen ion concentration, *i.e.*, $K_3[H^+] \gg 1$, eq 9 reduces to

$$\frac{-d[U(IV)]}{dt} = \frac{k_1'[U(IV)][Cl(III)]}{K_3[H^+]} \qquad (10)$$

Additional evidence that the hydrogen ion effect is real and not due to a medium effect is obtained from an attempt to fit the data to a Harned type equation[40] of the form

$$k_{obsd} = k\{\exp(\beta[H^+])\}$$

where β is an adjustable parameter. The resulting value of β is considerably larger than that expected for medium effects.[40]

D. The Inhibition of the Reaction between Uranium(IV) and Chlorine(III) by Chlorine(III).—The reaction is inverse first order in the hydrogen ion range of 0.75–1.50 *M*. A log–log plot of the pseudo-first-order rate constant multiplied by the hydrogen ion concentration as a function of chlorine(III) concentration has a slope of 0.96 at low chlorine(III) and 0.63 at high chlorine(III) concentrations. This implies that at low chlorine(III) concentration the reaction is first order with respect to chlorine(III) and at high chlorine(III) the order with respect to chlorine(III) concentration decreases. This again is indicative of

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[40] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963); *Inorg. Chem.*, **4**, 1166 (1965).

consecutive reactions which yield a rate expression of the type

$$\frac{-\mathrm{d}[\mathrm{U(IV)}]}{\mathrm{d}t} = k_{\mathrm{obsd}}[\mathrm{U(IV)}][\mathrm{Cl(III)}] = \frac{k_1''[\mathrm{U(IV)}][\mathrm{Cl(III)}]}{1 + K_2[\mathrm{Cl(III)}]} \qquad (11)$$

Again by choosing an appropriate value for K_2 such that $K_2[\mathrm{Cl(III)}] \ll 1$, eq 11 reduces to

$$\frac{-\mathrm{d}[\mathrm{U(IV)}]}{\mathrm{d}t} = k_1''[\mathrm{U(IV)}][\mathrm{Cl(III)}] \qquad (12)$$

E. The Form of the Rate Law.—The dependence of the observed second-order rate constant on both chlorine(III) and hydrogen ion concentrations was fitted to various general types of rate laws. The data in all cases were weighted by $[1/k_{\mathrm{obsd}}]^2$ which minimizes the per cent deviation between the experimental and calculated rate constants. The best fit of the data is given by the equation

$$k_{\mathrm{obsd}} = \frac{k_1}{(1 + K_2[\mathrm{HClO_2}])(1 + K_3[\mathrm{H^+}])} \qquad (13)$$

where $k_1 = 291.3 \pm 4.2\ M^{-1}\ \mathrm{sec}^{-1}$, $K_2 = 4.13 \pm 0.25$, and $K_3 = 20.8 \pm 3.2$. Values for the second-order rate constants were calculated in terms of eq 13. A comparison of these values with the experimentally observed rate constants is shown in Table I. The average deviation between the observed and calculated rate constants was less than 3.9%. In this context, it should be noted that alternate forms of the rate law included denominator terms such as $([\mathrm{H^+}] + K_2 \cdot [\mathrm{HClO_2}])$ and $(1 + K_2[\mathrm{ClO_2^-}])(1 + K_3[\mathrm{H^+}])$ and $1 + K[\mathrm{H^+}] + K_2K_3[\mathrm{Cl(III)}]$. The magnitude of the average deviation between the observed and calculated rate constant for these alternate models ranged from 12 to 15%. Clearly, eq 13 represents the best fit of the data.

F. The Effect of Temperature on the Rate of the Uranium(IV)–Chlorine(III) Reaction.—The results of a series of experiments at various temperatures and chlorine(III) and hydrogen ion concentrations are presented in Table I. In order to determine the activation parameters associated with k_1, the values of K_2 and K_3 must be known at the various temperatures employed.

Barnett[39] reported the thermodynamic quantities ΔG, ΔH, and ΔS for the association constant, K_3, of chlorous acid at zero ionic strength and 25° to be −2.67 kcal mol^{-1}, 4.10 kcal mol^{-1}, and 22.7 eu, respectively. The free energy for the computer-determined value for K_3 reported in this paper is estimated as −1.80 kcal mol^{-1} at 25° and an ionic strength of 2.00 M. Since the free energy also varies as a function of temperature, it is necessary to estimate the enthalpy and entropy associated with ΔG at 2.00 M ionic strength. Based on a number of assumptions,[41] these quantities were estimated and values for K_3 were calculated at the various temperatures. By employing the K_3 values for the various temperatures, computer-calculated values for k_1 and K_2 were determined. A listing of the values for these constants is given in Table II. Fitted k_{obsd} values obtained in this manner are listed in column 6 of Table I. The values of $\Delta H^{\pm}$ and $\Delta S^{\mp}$ for k_1 are 25.5 ± 0.3 kcal mol^{-1} and 38.1 ± 0.9 eu, respectively. The uncertainties represent computer-calculated standard deviations.

TABLE II

CALCULATED VALUES OF k_1, K_2, AND K_3 AS A FUNCTION OF TEMPERATURE

Temp, °C	k_1, M^{-1} sec^{-}	K_2, M^{-1}	K_3, M^{-1}	Av % dev[b]
25.0	291.3 ± 4.2	4.13 ± 0.25	20.8 ± 3.2	3.9
20.0	140.4 ± 3.2	3.24 ± 0.38	17.9[a]	3.8
55.0	62.2 ± 1.4	1.96 ± 0.30	15.5[a]	3.7
10.0	30.0 ± 0.8	1.29 ± 0.34	13.4[a]	4.5

[a] See ref 41 for a discussion of these values. [b] The average per cent deviation represents the difference between calculated and observed rate constants at that particular temperature.

G. Oxygen-18 Tracer Analysis.—The significance of the oxygen-18 tracer experiments is that a possible distinction between a one-electron and two-electron transfer process for the uranium(IV)–chlorine(III) reaction can be made. If a one-electron transfer process occurs, then a uranium(V) intermediate species would be produced. Since uranium(V) exchanges oxygen rapidly[42] with solvent, the resulting uranium(VI) product would contain oxygen atoms at the isotopic composition of the solvent. On the other hand, if uranium(VI) is produced directly *via* a two-electron atom transfer process, then one or both of the oxygen atoms of the uranium(VI) product would be derived from chlorine(III).

The results of this experiment, which are shown in Table III, indicate that oxygen is indeed transferred from chlorine(III) to uranium(VI). These results of high uranium(IV) concentrations are complicated by the reproportionation reaction

$$\mathrm{U^{4+} + UO_2^{2+} + 2H_2O \rightleftharpoons 2UO_2^{+} + 4H^{+}} \qquad (14)$$

which induces oxygen exchange in the uranium(VI) product. The formation of uranium(V) by means of eq 14 and the corresponding uranium(V) exchange reaction[19,42] increases the experimentally determined enrichment of the uranium(VI) and decreases the apparent transfer of oxygen from chlorine(III) to the

TABLE III

THE RESULTS OF THE EXTENT OF OXYGEN TRANSFER[a] FROM CHLORINE(III) TO URANIUM(VI) IN THE PRESENCE OF PHENOL

$R_{\mathrm{H_2O}}$	$R_{\mathrm{UO_2^{2+}}}$	$R'_{\mathrm{UO_2^{+}}}$	n_t[b]
3.346	2.835	2.442	0.77 ± 0.003[c]
4.298	3.542	2.963	0.81 ± 0.03[d]
3.982	3.383	2.923	0.71 ± 0.03[e]

[a] 0.214 M uranium (IV) and 1.00 M [H$^+$]. The meanings of the various columns are explained in the text. [b] The quantity n_t represents the number of oxygens transferred from chlorine(III) to uranium. [c] 0.215 M Cl(III) at 25°, complete reaction. [d] 0.215 M Cl(III) at 0°, complete reaction. [e] 0.151 M Cl(III) at 0°, less than 100% reaction.

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(41) In order to estimate the enthalpy and entropy for this process, first it was assumed that only the enthalpy was affected by an increase in ionic strength. By using a value of ΔG of −1.80 kcal mol^{-1} and a value of 22.7 eu for ΔS, ΔH was estimated as 4.97 kcal mol^{-1}. Second, it was assumed that only the entropy was affected by an increase in ionic strength. By employing values of −1.80 kcal mol^{-1} and 4.10 kcal mol^{-1} for ΔG and ΔH, respectively, ΔS was estimated as 19.8 eu. These estimates were used as limits and in the final analysis of the kinetic data, values of 4.54 kcal mol^{-1} and 21.2 eu for ΔH and ΔS, respectively, were used. These numbers represent average values for ΔH and ΔS for the evaluated limits for these two constants.

(42) G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **19**, 189 (1961); *Inorg. Chem.*, **1**, 69 (1962).

uranium product. To account for the increase in enrichment of the uranium(VI) due to the uranium(V) induced exchange, a blank correction experiment was carried out.

The number of oxygen atoms transferred from chlorine(III) to uranium was calculated by means of the equation[42]

$$n_t = \frac{2(R_{H_2O} - R'_{UO_2^{2+}})}{R_{H_2O} - R_{Cl(III)}} \tag{15}$$

where n_t is the number of oxygens transferred per uranyl ion which are derived from the oxidizing agent; R_{H_2O} represents the experimentally determined enrichment of the reaction solution; $R'_{UO_2^{2+}}$ represents enrichment of the uranyl ion corrected for the enrichment due to U(V)-induced exchange and calculated directly from $R_{UO_2^{2+}}$, the experimentally determined value; $R_{Cl(III)}$ is the enrichment of the oxidizing agent, chlorine(III), which is of normal enrichment (*i.e.*, 1.000). The result is that, on the average, 0.76 ± 0.04 oxygen is transferred from chlorine(III) to the uranium(VI) product.

Discussion

The predominant term in the observed rate law for the reaction between uranium(IV) and chlorine(III) in the presence of an excess of phenol indicates an inverse hydrogen ion dependence. This hydrogen ion dependence is in accord with the following net activation process

$$U_{aq}^{4+} + HClO_2 \rightleftharpoons [UClO_2^{3+}]^{\ddagger} + H^+ \tag{16}$$

A description of the net activation process in this manner is obtained from the rate law in terms of the principal species and shows the composition of the activated complex without regard to the detailed mechanism.[43]

The results of the tracer experiment yield quite convincing evidence that the reaction occurs *via* an inner-sphere process, in which the chlorine(III) oxygen must be directly bonded to the uranium(IV) in the activated complex. Since the tracer results indicate that on the average at least three-fourths of an oxygen atom is transferred from chlorine(III) to the uranium(VI) product, this strongly suggests that the principal pathway for the reaction must involve a two-electron atom transfer process.

The inverse hydrogen ion dependence and the overall inhibition of the reaction by chlorous acid suggests the mechanism

$$U^{4+} + HClO_2 \overset{K_2}{\rightleftharpoons} UOClOH^{4+} \tag{17}$$

$$H^+ + ClO_2^- \overset{K_3}{\rightleftharpoons} HClO_2 \tag{8}$$

$$U^{4+} + ClO_2^- \xrightarrow{k_1} \text{products} \tag{18}$$

The rate law for this mechanism can be written directly, since the chlorine(III) is in equilibrium with chlorous acid

$$[ClO_2^-] = [Cl(III)]/(1 + K_3[H^+])$$

and

$$[U^{4+}] = [U(IV)]/(1 + K_2[HClO_2])$$

Thus, the observed rate expression for this mechanism becomes

$$\frac{-d[U(IV)]}{dt} = \frac{k_1[U(IV)][Cl(III)]}{(1 + K_2[HClO_2])(1 + K_3[H^+])}$$

which is identical with the experimentally fitted form shown in eq 13.

Newton and Rabideau[43] have correlated the charge of the activated complex with the entropy of the activated complex for a number of actinide metal redox reactions. They have shown that the entropy of the activated complex can be related directly to the charge on the activated complex. The calculated entropy of the activated complex for the uranium(IV)–chlorine(III) reaction when calculated from $S°$ values for U_{aq}^{4+} of −80 eu and $HClO_2$ of 42 eu is about 0 eu.[44] Newton and Rabideau[43] reported an entropy for a 3+ activated complex of −30 ± 10 eu. In view of the fact that the comparison made by Newton and Rabideau was with systems involving simple electron exchange reactions of actinide metal ions, the disagreement is not at all surprising.

The rate of the uranium(IV)–chlorine(III) reaction, in the presence of 0.1 *M* phenol, is inhibited by chlorine(III). With high chlorine(III) concentrations, the value of the observed second-order rate constant is nearly 30% less than the rate constant observed at low chlorine(III) concentrations. Since the reaction is observed by monitoring a decrease in the absorbance of uranium(IV) as a function of time, a decrease in the observed rate constant would also be noted if chlorine(III) rapidly disappeared by a pathway other than the oxidation of uranium(IV) such that the effective chlorine(III) concentration should be less than the initial concentration used in the calculation. Some of the alternate pathways might be (1) the disproportionation of chlorine(III), (2) the reaction of chlorine(III) with phenol, or (3) the catalyzed disproportionation of chlorine(III) by uranium(IV) to form chlorine dioxide or chlorate ion.

The disproportionation reaction of chlorine(III) is well documented.[39,40,45–50] Kieffer and Gordon[46] reported a second-order rate constant of 1.17×10^{-2} M^{-1} for this process. Therefore, even at the highest chlorine(III) concentration employed in this study, the contribution from this pathway would be less than 1%. Likewise, the reaction of chlorine(III) with phenol[27,38] has a rate constant on the order of 0.035 M^{-1} sec^{-1}. At the highest chlorine(III) concentration used, the loss of chlorine(III) by this pathway would be less than 2%.

The reaction between vanadium(IV) and chlorine(III)[51] is observed to produce an abnormally large amount of chlorine dioxide. A preliminary conclusion from this observation is that the vanadium(IV) is catalyzing the disproportionation of chlorine(III) to form chlorine dioxide. To test this possibility in the present system, a solution containing 0.01 *M* urani-

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um(IV) and 0.4 M phenol was mixed with 0.01 and 0.3 M solutions of chlorine(III) in a Durrum–Gibson stopped-flow apparatus and the absorbance was monitored at 360 nm. At this wavelength chlorine dioxide exhibits an absorbance maximum with a molar absorptivity of 1250 M^{-1} cm^{-1}.

The maximum absorbance change observed for the 0.01 and 0.30 M chlorine(III) solutions is 0.040 and 0.200 absorbance unit, respectively. This increase in absorbance can be attributed either to the formation of chlorine dioxide or to the UO_2^{2+}–ClO_2^- complex.[52] If the absorbance increase is due entirely to chlorine dioxide, the effective decrease in chlorine(III) concentration would once again be less than 1%. Gordon and Kern[52] observed the formation of a charge-transfer complex between UO_2^{2+} and chlorite ion. The formation constant for the charge-transfer complex was assigned an approximate value of 0.02 M^{-1}. The molar absorptivity of this complex is estimated as 5×10^6 M^{-1} cm^{-1} at 360 nm. Since the uranium(IV) solution contained $\sim 10^{-3}$ M uranium(VI), the maximum concentration of the complex, assuming that the 0.20 absorbance unit change is due entirely to the complex, is calculated as 2×10^{-8} M. Based on this, the amount of chlorine(III) complexed is only 1×10^{-8} M.

It is obvious from these calculations that the effective decrease in chlorine(III) concentration would be less than 1% and nowhere near the required 30%. Therefore, the observed decrease in the rate cannot be attributed to a reduction in the effective chlorine(III) concentration by these pathways.

The observed absorbance change at 360 nm, attributed to the production of chlorine dioxide and/or the formation of a uranium(VI)–chlorite ion complex, does not preclude the possibility that the increase in absorbance is due to the formation of a uranium(IV)–chlorous acid complex.

A preference for a two-electron oxygen atom transfer in the reaction of uranium(IV) and oxygen-containing oxidizing agents has been established by Gordon and Taube.[42] Ondrus and Gordon[12,53] suggested that the preference for a one-electron transfer, by means of an inner-sphere process, appears to be associated with direct halogen bonding rather than oxygen bonding.

The most probable difference between reactions 16 and 17 would be the way in which the oxidizing agent is bonded to the uranium(IV). The reaction proposed in eq 17 would lead to products but that in eq 16 would not.

In the present system, the tracer study indicates that the principal pathway for the uranium(IV)–chlorine(III) reaction involves a two-electron oxygen-transfer process. This requires that the oxygen atom of the chlorite ion be bonded to uranium(IV) in the activated complex. The observed oxygen-transfer result rules out the possibility of a major contribution from the one-electron process. However, if chlorous acid is bonded to uranium(IV) by means of the chlorine atom, this is not inconsistent with the formation of a nonproductive intermediate such as is suggested by eq 16. This could account for the retardation of the rate of reaction by chlorous acid.

The reaction reported here is in accord with the mechanisms of other reactions of metal ions which involve the halogenate oxidants; that is, the two-electron transfer process appears to be associated with direct oxygen bonding in the first coordination sphere of the reductant.

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Tetraalkylammonium Pentacyanocobaltates. Their Preparation, Properties, and Reactivity

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Conductivity, spectral, electrochemical, and magnetic measurements on tetraalkylammonium cyanide–cobalt(II) chloride mixtures in acetonitrile solution are discussed and indicate the presence of the species $(CH_3CN)_2Co(CN)_2$, $[CH_3CNCo(CN)_3]^-$, and $[Co(CN)_5]^{3-}$, in relative concentrations dependent on the $[CN^-]/[Co]$ ratio. The latter ion has been isolated as the solid complexes $(R_4N)_3[Co(CN)_5]$ (Ia, R = C_2H_5; Ib, R = n-C_4H_9). The reactions of compounds I are discussed in relation to those of aqueous solutions of $M_3[Co(CN)_5]$ (II, M = alkali metal), previously studied by other workers. Reaction of compounds I with oxygen gives $(R_4N)_3[Co(CN)_5O_2]\cdot 1.5H_2O$ (IIIa, R = C_2H_5; IIIb, R = n-C_4H_9).[2]

The pentacyanocobalt(II) ion,[3,4] $[Co(CN)_5]^{3-}$, has been much investigated in recent years because of its behavior as a homogeneous hydrogenation catalyst.[5-8] Typically, solutions containing this ion are prepared by reaction of a cobalt(II) compound with an alkali metal cyanide. As noted by Kwiatek,[6] previous studies

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(2) Because of the interest in the pentacyanocobalt(II) ion, samples of compound Ia and also of compound IIIa have been sent to Dr. J. J. Daly, Monsanto Research, S.A., Zürich, Switzerland, for determination of their crystal and molecular structures.

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