influence of O attachment should be to decrease Δ for M–O–SO complexes, thus enhancing the influence of the primary force constant changes. The trends in off-diagonal force constants and their resulting influence on the value of Δ is less readily predicted. It does appear, however, that the increase in Δ upon O coordination is likely to be a general phenomenon and therefore a useful diagnostic feature for the mode of SO_2 coordination. These trends in Δ are not intended for application to compounds containing 4-coordinate sulfur such as sulfuryl halides or sultones.

Application of the above systematics to recent infrared data for adsorbed SO_2 implies that attachment to the surface generally occurs through sulfur.[12] One exception is the study by Deno et al. of SO_2 absorbed at elevated temperatures on Al_2O_3, where very large separation of the SO stretches is reported. In this case, however, the unusually high frequencies of the modes attributed to SO_2 do not fit well with previous observations on SO_2 complexes, so structural speculations are not justified. The Δ criterion also may be applied to the recently prepared compound $(C_6H_5)_3InSO_2$, for which Hsieh and Deacon favor an O-bonded structure $(C_6H_5)_3InOSO$.[13] The value of Δ calculated from their data, 199 cm^{-1}, agrees with the postulated In–O bond formation but in the absence of molecular weight data more complex structures cannot be excluded.

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Kinetics and Mechanism of the Oxidation of Uranium(IV) by Hypochlorous Acid in Aqueous Acidic Perchlorate Media

ROBERT A. SILVERMAN and GILBERT GORDON*

The oxidation of uranium(IV) by hypochlorous acid has been studied in aqueous sodium perchlorate–perchloric acid solutions. The reaction $U^{4+} + 2HOCl = UO_2^{2+} + Cl_2(aq) + 2H^+$ proceeds appropriate to the rate law $-d[U(IV)]/dt = k_0 \cdot [U^{4+}][HOCl][H^+]^{-1}$. At 25° and 3 M ionic strength, k_0 is 1.08 ± 0.07 sec^{-1}. Over the 1–25° temperature range, $\Delta H^\ddagger$ is 18.4 ± 0.1 kcal mol^{-1}, and $\Delta S^\ddagger$ is 3.1 ± 0.4 eu. The inverse hydrogen ion dependence of the rate law is explained by a rapid preequilibrium, in which a proton is lost from one of the reactants. A uranyl-like activated complex, $[H_2UO_2Cl^{3+}]^\ddagger$, is suggested, with one proton likely to be residing on each oxygen atom. Evidence is presented that the mechanism involves a two-electron transfer, with the intermediate chloride ion rapidly reacting with hypochlorous acid to form chlorine. The uranium(IV)–hypochlorous acid reaction plays an important role in the oxidation of uranium(IV) by aqueous chlorine solutions. The magnitude of this role was seriously underestimated by previous investigators.

Introduction

Both aqueous chlorine(0) and chlorine(I) are transient intermediates in the complex reactions of chlorine(III) with various metal ions such as vanadium(IV)[1] or uranium(IV).[2,3] The studies of many reactions of aqueous chlorine(0) are complicated by the accompanying chlorine(I) reactions, which arise from the equilibrium

$$Cl_2(aq) + H_2O = HOCl + H^+ + Cl^- \qquad (1)$$
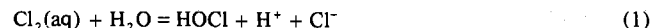
At 25° and zero ionic strength,[4] the equilibrium constant for reaction 1 is 3.94×10^{-4} M^2 and its variation with ionic strength is reported elsewhere.[5] Dreyer and Gordon[6] studied the reactions of vanadium(IV) with aqueous chlorine(0) and chlorine(I) and determined the rate of the reaction with the

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aqueous Cl_2 species by correcting for that portion of the reaction due to chlorine(I).

The kinetics of the reaction[7,8]

$$U^{4+} + Cl_2(aq) + 2H_2O = UO_2^{2+} + 2Cl^- + 4H^+ \qquad (2)$$
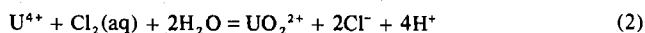
and the kinetics of the analogous reactions with aqueous iodine(0)[8] and bromine(0)[9] all display a term in the rate law which is inverse second order in hydrogen ion. In a preliminary survey, Gordon and Feldman[2] found the reaction with chlorine(I)

$$U^{4+} + 2HOCl = UO_2^{2+} + Cl_2(aq) + 2H^+ \qquad (3)$$
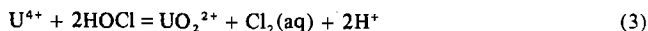
to be much more rapid. Adegite and Ford-Smith[8] attempted to estimate the rate of uranium(IV)–chlorine(I) reaction by studying the dependence of the rate of the corresponding uranium(IV)–chlorine(0) reaction on the concentration of

chloride ion, but their results are in sharp disagreement with those of Gordon and Feldman.[2]

The uranyl ion, UO_2^{2+}, exchanges its oxygen atoms with solvent water extremely slowly.[10] This oxygen exchange is markedly catalyzed by micromolar traces of uranium(V), because of the rapid electron transfer between the UO_2^{2+} ion and the UO_2^+ ion and the oxygen lability[10] of UO_2^+. This can be used to provide a sensitive test for the presence of traces of uranium(V) and thus for whether an oxidation reaction of uranium(IV) is proceeding by a direct two-electron-transfer process or by two successive one-electron transfers. In the oxidation of uranium(IV) by O_2,[11] H_2O_2,[11] or $HClO_2$,[3] labeled oxygen from the oxidant appears in the uranyl ion product. Because of the substitution lability of uranium(V), this oxygen transfer can be used as evidence that these oxidation–reduction reactions involve a two-electron-transfer mechanism.

The isotopic exchange reactions of chlorine(I) with labeled chloride ion[12] and with oxygen-labeled water[13] have been studied in basic solution.[14] Chlorine(I) transfers labeled oxygen to sulfite ion[15] and nitrite ion[13] in these two-electron oxidation–reduction reactions. A two-electron mechanism has also been postulated in the oxidation of iron(II)[16] and chromium(II)[17] by chlorine(I), due to the dimeric nature of the metal(III) ions formed.

Ondrus and Gordon[18] studied the oxidation of tris(1,10-phenanthroline)iron(II) by aqueous chlorine(0) and chlorine(I). They observed that the chlorine(I) reaction was slower than that of chlorine(0) and proceeded by two parallel paths: an outer-sphere, one-electron path and an inner-sphere, two-electron path.

Chlorine(I) is generally a much more rapid oxidant than chlorine(0). There are two important exceptions to this rule, both involving the one-electron reduction of chlorine(0): (a) A Cl_2^- or $Cl\cdot$ intermediate can be rapidly produced from aqueous Cl_2 molecules by a very powerful one-electron reductant, such as vanadium(III)[19] or chromium(II).[17] (b) The complexation of the central reductant ion forces the oxidation to proceed by an outer-sphere, one-electron mechanism.[18,20]

Experimental Section

Solutions. An $\sim$8 M sodium perchlorate stock solution was prepared[2,9] from the triply recrystallized salt, which had been synthesized from sodium carbonate and perchloric acid. Stock solutions of $\sim$0.6 M uranium(IV) perchlorate in 1–2 M perchloric acid were prepared by the potentiostatic reduction of acidic uranyl perchlorate solutions.[2]

The uranium(IV) stock solutions, stored refrigerated under an atmosphere of nitrogen, were quite stable, with less than 5% decomposition to uranyl ion after several years. The uranium(IV) concentration was determined with a Cary 14 spectrophotometer immediately prior to use. The molar absorptivity[9] of the main visual peak, at 648 nm, is 60.0 M^{-1} cm^{-1}. The 350–400-nm region was also checked to ensure that the uranyl ion concentration was less than 5% of the uranium(IV) concentration.

Chlorine monoxide solutions were prepared by the method of Cady.[21] The clear solution of chlorine monoxide was decanted from the mercuric oxychloride residue, and it could usually be stored several weeks in the freezer compartment of a refrigerator with no detectable formation of chlorine. Hypochlorous acid solutions were prepared shortly prior to their use by the aquation reaction

$$Cl_2O(\text{in } CCl_4) + H_2O = 2HOCl(aq) + CCl_4 \text{ layer} \qquad (4)$$
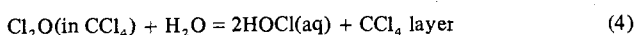
followed by the separation of the aqueous and carbon tetrachloride layers. The concentration of hypochlorous acid was determined spectrophotometrically.[5] In the temperature-dependence series of runs, the oxidizing power of the hypochlorous acid solution was determined by iodometric titration.

Except for one run at 1 M ionic strength, all of the kinetic runs were adjusted to 3 M ionic strength by the appropriate concentrations of sodium perchlorate and perchloric acid.

Distilled water which had been passed through a Barnstead mixed-bed deionizing column was used for all experiments. Except

for the special preparations noted above, reagent grade chemicals were used without further purification. Potassium iodate and potassium acid phthalate were the primary standards for redox and acid–base determinations, respectively. Where possible, glass syringe-pipets[22] were used to measure precisely all critical volumes less than 15 ml. Standard titration techniques were employed, except that, wherever practical, the bulk of the titrant was dispensed by glass syringe-pipets, and the titration was finished with a microburet. With this method, precisions of ±0.1% were routinely achieved, even with very small volumes. This technique was particularly adapted to the iodometric titration in situ of the volatile oxidants, chlorine, and hypochlorous acid, contained in a Cary spectrophotometric cell.

Stopped-Flow Procedure. A Gibson-Durrum stopped-flow spectrophotometer was maintained at 25° by means of a circulating thermostat. A Tektronix Model 564 storage oscilloscope was used to record the kinetic traces. In the runs with excess hypochlorous acid, the monochromator was set at 648 nm, where only uranium(IV) absorbs. Excellent pseudo-first-order rate law fits were obtained from 0 to $\sim$90% reaction, the last measurable data point. The observed infinite-time readings were in reasonable agreement with the computer-fitted values of $A\infty$.

In the runs with excess uranium(IV), the monochromator was set at 355 nm, a compromise wavelength sensitive mainly to the changing chlorine concentration. The absorbance at this wavelength rose to a maximum within 3–9.5 sec, depending on the acidity, and then slowly declined. The rising portion represents the reduction of hypochlorous acid to a hydrolyzed chlorine solution, and the declining part represents the slow reaction of this chlorine solution with the excess uranium(IV). The kinetic trace that was measured to calculate the rate constant for the uranium(IV)–hypochlorous acid reaction displays the absorbance rising from its initial value until it just passes through its maximum.

Temperature Dependence Runs. The rapid-mixing syringe of Thompson and Gordon[23] was employed for a series of nine runs in 3 M perchloric acid at various temperatures. The spring-driven syringe forcefully injected 0.295 ml of 0.140 M uranium(IV) solution into 5.984 ml of $\sim$0.08 M hypochlorous acid solution contained in a 2-cm Cary cell. The resulting turbulence rapidly mixed the two solutions, resulting in a fivefold excess of hypochlorous acid.

Both solutions were spectrophotometrically assayed before the first run, and the hypochlorous acid solution was titrated iodometrically. Any loss of oxidant titer was due to the volatility of hypochlorous acid and not to its decomposition.

All critical volumes, except for the rapid injection of the uranium(IV) solution, were determined at ambient temperature. The concentrations reported here have been corrected to the actual temperature of the kinetic runs, using the known[24] temperature–density relationships of aqueous perchloric acid. Temperature control was maintained by a circulating thermostat. Within a given run, the temperature were constant to ±0.5° at 1° and to ±0.1° at the higher temperatures.

Six of the runs were performed at 647.2 nm, the wavelength of maximum uranium(IV) absorbance on the Cary 14, and three of the runs were at 355 nm. In addition, dummy runs were performed at each temperature, injecting uranium(IV) solution into 3 M perchloric acid containing no hypochlorous acid. Within 2–9 sec after injection, the 647.2-nm absorbance became stable to within ±2 milli absorbance units of its final value. This mixing time includes the time necessary to withdraw the syringe needle from the septum. These dummy runs also provided information on the baseline absorbance at 355 nm and on the amount of uranium(IV) actually being injected.

Results

The reaction of uranium(IV) with hypochlorous acid follows the stoichiometry of eq 3 and obeys the general rate law

$$-\frac{d[U(IV)]}{dt} = k_0 \frac{[HOCl][U^{4+}]}{[H^+]} = k_0 \frac{[HOCl][U(IV)]}{[H^+] + K_{UOH}} \qquad (5)$$

where the total uranium(IV) concentration, $[U(IV)]$, is the sum of the concentrations of the two ionic species, $[U^{4+}]$ and $[UOH^{3+}]$, in rapid equilibrium

$$U^{4+} + H_2O = UOH^{3+} + H^+ \qquad (6)$$

At 25°, K_{UOH}, the equilibrium constant for this equation, is

Table I. Rate Constants for the Reaction between 3.4 mM Uranium(IV) and Excess Hypochlorous Acid at 3.0 M Ionic Strength and 25°

[HClO$_4$] (av), M	1.007^a	0.509$_5$	1.007	1.007	2.00$_3$	2.99$_7$
[HOCl] (av), mM	182.8	185.4	184.5	101.4	208.3	191.8
% Cl$_2$	1.4 ± 0.1	0.2 ± 0.1	1.2 ± 0.3	2.1 ± 0.3	1.4 ± 0.2	0.0 ± 0.2
k' (fitted), sec^{-1}	0.267 ± 0.9%	0.387 ± 1.4%	0.207 ± 0.8%	0.111 ± 0.9%	0.116 ± 1.8%	0.0717 ± 1.3%
σ_A, mA	±0.9	±2.0	±1.9	±1.0	±2.8	±1.3
k_0, sec^{-1}	1.51	1.11	1.15	1.12	1.13	1.13

^{a} 1.04 M ionic strength.

0.028 and 0.021 M at, respectively, 1 and 3 M ionic strength.[25]

The general rate constant, k_0, is related to the observed pseudo-first-order rate constants by the equation

$$-\frac{d[U(IV)]}{dt} = k_0 \frac{[HOCl][U(IV)]}{[H^+] + K_{UOH}} \equiv k'[U(IV)] \equiv$$
$$k''[HOCl] \qquad (7)$$

where k' and k'', respectively, were utilized in the analysis of the data from the runs with excess hypochlorous acid and the runs with excess uranium(IV).

A. Uranium(IV) with Excess Hypochlorous Acid. The results of a series of reactions in which uranium(IV) reacted with a 15- to 30-fold excess of hypochlorous acid in a series of stop–flow runs at 25° and 648 nm, where only the uranium(IV) contributed significantly to the absorbance change, are given in Table I. The values tabulated for the concentrations of hydrogen ion and hypochlorous acid are those calculated to exist at midreaction.

The absorbance vs. time data served as input to a nonlinear least-squares computer program[26] utilizing a subroutine based on the first-order rate law. This program also calculates the standard deviation of each fitted parameter, as well as the standard deviation of the individual absorbance measurement, σ_A. The experimental value of A_0, the zero-time absorbance, was treated as a fixed input parameter, while k' and A_∞ were simultaneously fitted to the data.

The best estimate of σ_A, obtained by pooling the variances from the six kinetic runs is ±2 milli absorbance units. Similarly pooled, the standard deviation of the pseudo-first-order rate constant, k', is ±1.3%. The fitted values of A_∞ averaged 7 ± 7 milli absorbance units greater than the values of A_∞ measured on the oscilloscope several half-lives after the last data point. Ideally, at this wavelength, A_∞ should be zero. Because of the various experimental difficulties associated with the stop–flow technique, the infinite values of A_∞ are not surprising, nor are they sufficient to interfere with a satisfactory determination of the pseudo-first-order rate constant.

The value of k_0, calculated from eq 7, is 1.13 ± 0.01$_6$ sec^{-1} at 3 M ionic strength, and 1.3$_4$ times this rate at 1 M ionic strength. The contribution from the K_{UOH} term is minor, ranging from 0.7 to 4%. In the series of runs at 3 M ionic strength, the scatter in k_0 appears to arise solely from the random scatter of the absorbance–time data.

B. Hypochlorous Acid with Excess Uranium(IV). In order to confirm that the reaction is first order in both uranium(IV) and hypochlorous acid, a series of kinetic runs was performed in the presence of a great excess of uranium(IV), at 355 nm. This wavelength is optimal for monitoring the concentration of the aqueous Cl$_2$ species, with minimal interference[27] from uranium(VI).

Stoichiometrically, the reaction can be considered in two stages: stage I, corresponding to eq 3, where the hypochlorous acid is reduced to a highly hydrolyzed chlorine solution, and stage II, corresponding to eq 2, where this chlorine solution is reduced to chloride ions. Kinetically, however, the direct reaction between uranium(IV) and aqueous Cl$_2$ molecules is so slow[7,8] as to be almost negligible, and the rate of the overall reaction in *both* stages depends *mainly* upon the rate of the

Table II. Rate Constants for the Reaction of Hypochlorous Acid with Excess^a Uranium(IV) at 3.0 M Ionic Strength and 25°

[HClO$_4$] (av), M	0.385	0.385	0.534	0.535	0.760	0.982
[U(IV)] (av), mM	100.8	100.8	100.8	99.2	100.7	100.7
[HOCl]$_0$, mM	3.0	3.0	3.0	12	3.0	3.0
$10^4 K_{Cl_2}$,^{b} M^2	1.94	1.94	1.48	1.48	1.42$_5$	1.35$_5$
k'', sec^{-1}	0.278	0.288	0.203	0.202	0.149$_3$	0.118$_4$
k_0, sec^{-1}	1.11$_4$	1.15$_4$	1.11	1.12$_6$	1.15	1.17

^{a} [U(IV)]$_0$ = 101.$_2$ mM. ^{b} K_{Cl_2} calculated from formulas and data given in ref 5 where the variation of K_{Cl_2} is reported as a function of solution composition at constant ionic strength.

Table III. Uranium(IV)–Hypochlorous Acid Reaction as a Function of Temperature in 3 M Perchloric Acid

Temp, °C	[HClO$_4$], M (at T°C)	[HOCl]$_0$, mM	[U(IV)]$_0$, mM	$10^2 k_0'$, sec^{-1}	
				Exptl^c	Fitted
0.7^a	3.02	74.6	7.24	6.10 ± 0.1$_5$	5.96
1.65^a	3.02	74.3	6.81	6.53 ± 0.1$_3$ ±	6.72
7.5^a	3.01	73.6	6.96	13.80 ± 0.1$_6$	13.84
7.4^a	3.01	73.6	6.87	13.91 ± 0.1$_0$	13.67
7.4$_7$^{b}	3.01	73.2	6.68	13.96 ± 0.4$_0$	13.79
15.8$_7$^{a}	2.99	72.9	6.62	36.5 ± 0.2	37.0
15.9$_2$^{b}	2.99	72.9	6.28	36.5 ± 0.3	37.2
25.0$_3$^{a}	2.98	72.5	6.06	102.1 ± 0.3	102.0
25.0$_7$^{b}	2.98	72.3	6.18	104.0 ± 0.4	102.5

^{a} Measured at 647.$_2$ nm. ^{b} Measured at 355 nm. ^{c} The uncertainties correspond to one standard deviation and are reported in terms of percent.

uranium(IV)–hypochlorous acid reaction. At any given moment, the concentrations of hypochlorous acid and chlorine are related by the relatively rapid equilibrium[28] shown by eq 1.

At the boundary between stages I and II, both the absorbance at 355 nm and the chlorine concentration reach their maximum values. It can be shown that,[5] at this point, the concentration of hypochlorous acid is equal to that of the chloride ion, just as would be the case in a pure aqueous chlorine solution. The overall absorbance changes were in reasonable agreement with the values predicted from the molar absorptivities of the individual species. The long-time traces, displaying the kinetics of state II, were not subjected to detailed analysis, but their shape agreed with the expected[7] behavior of uranium(IV) reacting with hydrolyzed chlorine solutions.

The mathematical details of the excess-uranium(IV) case are cumbersome and are given elsewhere.[5] The final results are given in Table II. The average value of k_0 is 1.14 ± 0.02$_4$ sec^{-1}, which is in excellent agreement with the results obtained in the presence of excess hypochlorous acid.

C. Temperature Dependence. In order to determine the activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, a series of runs was carried out from 0.7 to 25° and the results are shown in Table III.

In a given run, the acid concentration remained relatively

Table IV. Summary of Values for k_0 at 3 M Ionic Strength and 25°

	k_0, sec^{-1}	[HO-Cl]$_0$, M	[U(IV)]$_0$, M	[H$^+$], M	Comments
A	1.13 ± 0.01$_6$	0.1 to 0.2	0.003	0.5–3	Durrum stop-flow, excess HOCl
B	1.14 ± 0.02$_4$	0.003–0.012	0.101	0.385–0.982	Durrum stop-flow, excess U(IV)
C	1.03 ± 0.01	0.07	0.007	3.0	Rapid-mix, Cary 14 0.7–25°C range
D	1.08 ± 0.07				Average of lines A and C

constant, so the second-order subroutine of the nonlinear least-squares program[26] was used to fit the absorbance–time data. This data, typically 40–80 points per run, extended from the first points that were readable after the uranium(IV) injection to >95% reaction. The parameters k_0', A_0, and A_∞ were simultaneously fitted where k_0' is defined as

$$-\frac{d[U(IV)]}{[dt]} = k_0' \frac{[HOCl][U(IV)]}{[H^+]} \qquad (8)$$

The experimental value of A_∞(obsd) was not employed as a fixed input parameter in that, under these conditions, the long-time points appeared to excercise an undue influence on the value fitted to k_0'. These long-time points are more vulnerable to error from drifts in the "blank" absorbance and from volatility losses. In general, the fitted values of A_∞ differed by less than 0.003 absorbance unit at 647 nm from the observed values.

The value of [U(IV)]$_0$ was calculated[5] from the known molar absorptivities and from the net absorbance change. Because of the fivefold excess of hypochlorous acid, the value assigned to [U(IV)]$_0$ is not critical: a 25% error in its estimation would lead to a miscalculation of only 1% in k_0'.

The activation parameters were fitted[26] to the data shown in Table III using weights of $[1/k_0']^2$ in an attempt to minimize the average percent error. The fitted activation parameters are 18.3$_8$ ± 0.1$_2$ kcal mol^{-1} for $\Delta H^\ddagger$ and 3.1$_4$ ± 0.4$_3$ eu for $\Delta S^\ddagger$.

The values of k_0'(fitted) in Table III were calculated from these activation parameters and the temperature of the run. The average percentage discrepancy between this value and the input value of k_0' is ±1.9%. This interrun imprecision, arising in the fitting of the activation parameters, is an order of magnitude poorer than the intrarun imprecision in k_0'. It can most reasonably be explained by small uncertainties in the temperatures and the values of [HOCl]$_0$.

The contribution of the K_{UOH} term in eq 7 is only 0.7% at 25° and is even less at lower temperatures. Thus at 25° and 3 M ionic strength, k_0' is calculated to be 1.02$_5$ ± 0.01 sec^{-1} and, from eq 7, k_0 corresponds to 1.03 ± 0.01 sec^{-1}.

Summary of Results. The results of the three series of experiments for the uranium(IV)–hypochlorous acid reaction are summarized in Table IV. The rate constant on line C is probably the most accurate one, due to more accurate absorbance measurements and better control of the temperatures and concentrations on the Cary 14 spectrophotometer.

On the other hand, the rate constants from the experiments with excess uranium(IV) are not as reliable, due to the many approximations required in their derivation. The almost exact agreement between lines A and B appears to be fortuitous but does strongly confirm the form of the rate law given by eq 5.

It is our judgment that the best estimate of the numerical value of k_0 is obtained by averaging the results on lines A and C. Thus, k_0 is 1.08 ± 0.07 sec^{-1} at 25° and at 3 M ionic strength and $\sim$1.3$_4$ times this value at 1 M ionic strength.

Discussion

The result reported here confirms the earlier observations of Gordon and Feldman.[2] Adegite and Ford-Smith[8] observed that the rate of the reaction of uranium(IV) with hydrolyzed chlorine solution is

$$-\frac{d[U(IV)]}{dt} = k_{Cl_2} \frac{[Cl_2][U^{4+}]}{[H^+]^2} + k_0 \frac{[HOCl][U^{4+}]}{[H^+]}$$

where k_{Cl_2} is $\sim$0.012 M sec^{-1} at 25° and 2.5 M ionic strength. It would appear that they somewhat underestimated the contribution of the second term, perhaps because of a paucity of points below 0.2 M chloride ion. Thus their reported values of k_{Cl_2} are approximately 10–20% too high and their discussion of the effect of added chloride ion should be read with considerable caution.

If the oxidation of uranium(IV) by hypochlorous acid involved a one-electron transfer, the initial products would be two reactive intermediates: uranium(V) and some type of chlorine(0) radical. This would lead to a chain reaction, which, unless the chain-breaking steps are extremely rapid, is not supported by the simple formulation of the rate law. To the contrary, one of the necessary chain-breaking steps, the disproportionation of uranium(V), is known to be only moderately rapid.[29]

Gordon and Persoon[30] studied the H$_2$O*–UO$_2^{2+}$ isotopic oxygen exchange reaction in the presence of the ongoing uranium(IV)–hypochlorous acid reaction. They demonstrated that the concentration of the UO$_2^+$ ion, which would catalyze this exchange reaction,[10] was less than 2 × 10^{-6} M during the course of the redox reaction. From this result, it may be inferred that the major pathway does not correspond to a one-electron-transfer process.

Thus, the principal pathway must correspond to a two-electron-transfer process

$$U^{4+} + HOCl + H_2O = UO_2^{2+} + Cl^- + 3H^+ \qquad (9)$$
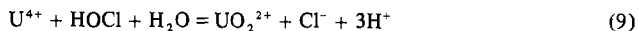
where the intermediate product chloride ion rapidly[28] reacts with hypochlorous acid to form chlorine(0). Under these reaction conditions, this should give rise to an apparent "induction" period in the formation of chlorine(0) of $\sim$0.01 sec at 355 nm, owing to the relative slowness of the formation of the aqueous chlorine(0) species.
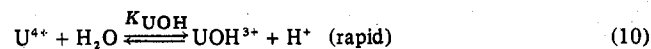
The short-time kinetic traces (typically 100 msec full scale) were examined for any evidence of an induction period, but none could be detected, due mainly o the small total absorbance change that occurred in this time period. The concentrations had been optimal for the determination of the rate constant and not at all suitable for the detection of an induction period.

The optimal conditions for observing an induction period in the formation of chlorine would be (a) 0.1–1.0 M ionic strength, so that K_{Cl_2} would be greater[5] than 6 × 10^{-4} M^2, (b) hydrogen ion concentration below $\sim$0.2 M, in order to slow the recombination of hypochlorous acid and chloride ion,[28] and (c) sufficient concentrations of hypochlorous acid and uranium(IV), so that the absorbance change in the first $\sim$0.1 sec will be well above the noise level. If these rather difficult experimental conditions can be met, induction periods as long as 30 msec can be expected, with a noticeable break in the 355-nm kinetic trace which can be compared to one produced at a longer wavelength, sensitive only to the uranium(VI): uranium(IV) concentration ratio, which should display no break or induction period.
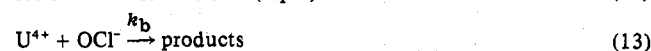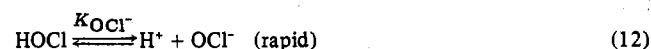
It may be inferred from the rate law reported in eq 5, that the empirical composition of the activated complex is $(UOCl^{3+})^\ddagger$, with an unknown degree of hydration. A reasonable conjectured structure would incorporate one water molecule into the activated complex, resulting in the structure

$[HO-U-OH-Cl^{3+}]^{*}$, with the exact positions of the protons uncertain. This $O-U-O$ configuration, which simulates the structure of both uranium(V) and uranium(VI), has been frequently postulated in actinide reactions.[31]

Although the composition of the activated complex is specified by the observed rate law, its mode of formation is consistent with several kinetically indistinguishable mechanisms. The first mechanism (a) is

$$U^{4+} + H_2O \xrightleftharpoons{K_{UOH}} UOH^{3+} + H^+ \quad \text{(rapid)} \tag{10}$$

$$UOH^{3+} + HOCl \xrightarrow{k_a} \text{products} \tag{11}$$

where $k_0 = k_a K_{UOH}$. From the reported[25] values of K_{UOH}, k_a is calculated to be 54 M^{-1} sec^{-1} at 3 M ionic strength and 25°. From the value of the enthalpy of uranium(IV) hydrolysis,[25] ΔH_a^{*} associated with k_a is calculated to be $\sim$7 kcal mol^{-1}. The second mechanism (b) is

$$HOCl \xrightleftharpoons{K_{OCl^-}} H^+ + OCl^- \quad \text{(rapid)} \tag{12}$$

$$U^{4+} + OCl^- \xrightarrow{k_b} \text{products} \tag{13}$$

where $k_0 = k_b K_{OCl}$. From the reported[32] value of K_{OCl^-} and its enthalpy, k_b is calculated to be $\sim$4 × 10^7 M^{-1} sec^{-1}, with an associated ΔH_b^{*} of $\sim$14.5 kcal mol^{-1}.

The third possibility would involve a rapid equilibrium yielding trace amounts of a deprotonated metastable complex ion, $UOCl^{3+}$, which could decay to the products by means of a rate-determining first-order process. Since such a complex escaped detection, this mechanism would appear to be less likely than either of the other two.

Mechanisms a and b appear equally reasonable. It should be noted, however, that ΔH_b^{*} corresponds to an unusually large heat of activation for a process having a rate constant as large as k_b.

The proposed inner-sphere nature of the activated complex and the resulting two-electron-transfer mechanism is supported by the oxygen-18 tracer study and by the fact that hypochlorous acid attacks uranium(IV) much more rapidly than does chlorine. In this context, it should be noted that there does not appear to be any experimental confirmation of an outer-sphere two-electron-transfer process.[33] In oxidations where the inner sphere of the reducing agent remains intact, hypochlorous acid attacks more slowly than chlorine, and often by a different mechanism.[18]

The role of the proton in oxidations of uranium(IV) has attracted considerable interest.[31] In the case of reactions with chlorine, bromine or iodine, two protons are lost in the formation of the $O-U-O$ core of the activated complex.[8,9] In the case of hypochlorous acid, this two-oxygen requirement is filled by the loss of a single proton from the reactants. This is consistent with the generalization that the loss of a proton from one of the water molecules in the hydration sphere of the U^{4+} ion facilitates the bonding of the oxygen of that water molecule to the central atom in the formation of the uranyl-like $O-U-O$ configuration.[31]

References and Notes

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