Sb, 31.07, 31.04. In contrast to the salts of the other ions of the series, dimethyldiphenylantimony salts are quite unstable. The tetrafluoroborate salt must be recrystallized from water immediately before use. The tetrafluoroborate salt loses boron trifluoride and methyl fluoride to form diphenylmethylantimony.

Polarographic data were taken on a locally constructed operational amplifier polarograph. A three-electrode system was used with a saturated calomel reference electrode. The cell was maintained at 25° and the solution blanketed with prepurified nitrogen during each run. The solutions were deaerated for 15 min with prepurified nitrogen before each polarographic run. All background solutions were prepared from distilled water and reagent grade chemicals. Potassium nitrate was used as the supporting electrotype. The solutions were buffered at pH 10.2 using carbonate buffer. It was necessary to work at this pH to obtain sufficient separation of the second wave from hydrogen reduction. All polarograms and coulometric runs were made at this pH unless otherwise noted. Concentration of the electroactive species was generally 2×10^{-3} M. All polarographic and coulometric solutions contained 0.01% Trition X-100.

Cyclic voltammetry was done at a hanging mercury drop on a Kemula electrode (Brinkman Instruments). Low-frequency scans were recorded on an X–Y recorder while high-frequency measurements were photographed from an oscilloscope trace. A Wavetek Model 112 signal generator was used to generate the triangular wave.

Large-scale controlled-potential electrolyses were carried out on a mercury pool using a potentiostat constructed in these laboratories. The coulometric cell had a nominal working electrode area of 30 cm². The mercury was agitated with a magnetic stirrer. The anode was isolated in a separate chamber behind a fritted glass disk. The reference electrode was positioned directly above the working electrode to minimize the effect of solution resistance. The solution compositions were the same as those used for polarography. Prepurified nitrogen was bubbled through the solution for about 15 min before each electrolysis, and the cell was sealed to eliminate the possibility of loss of the various products. All connections to the cell were made through ground-glass joints.

Product analysis was done by nuclear magnetic resonance spectroscopy on a Varian T-60 spectrometer. After electrolysis 2 ml of $CDCl_3$ was injected into the electrolysis cell under an argon atmosphere. The electrolysis solution and the $CDCl_3$ were then stirred for 30 min. The mixture of aqueous electrolysis solution, $CDCl_3$, and mercury was transferred to a modified separatory funnel and the $CDCl_3$ removed through a septum. Evaporation of the $CDCl_3$ from a known volume of the extract showed recovery of the products was 95–100% complete. The product distributions could be obtained by taking the ratios of the areas of the phenyl and methyl peaks obtained by nmr. The mixtures gave very well-defined spectra, and no interferences from the Trition X-100 were noted.

Control experiments were carried out to verify that no exchange of groups occurs between the antimony and mercury compounds. Equimolar amounts of diphenylmercury and tetramethylantimony iodide were introduced into electrolysis. The tetramethylantimony ion was then reduced under the conditions of the other electrolyses. The products were extracted into $CDCl_3$ and analyzed by nmr as previously described. No exchange of groups between the antimony and mercury was noted. Methylmercury chloride was reduced to dimethylmercury in the presence of triphenylantimony to check another possible redistribution. Assay by nmr showed no redistribution in this case either. As a check on the stability of the unsymmetrical products, dimethylphenylantimony was prepared and placed in the electrolysis cell along with phenylmercury acetate. The phenylmercury acetate was reduced to diphenylmercury and the electrolysis solution analyzed as before. Careful examination of the nmr spectra showed that no decomposition of the dimethylphenylantimony had taken place. This control was repeated using methylmercury chloride in place of the phenylmercury acetate. Following the electrolysis an assay of the solution showed no decomposition of the dimethylphenylantimony.

Synergistic Effect of Tri-*n*-octylamine on the Solvent Extraction of Cerium(III) by Thenoyltrifluoroacetone[1]

By L. Newman* and P. Klotz

The synergistic effect of tri-*n*-octylamine (R_3N) on the solvent extraction of cerium by thenoyltrifluoroacetone (HT) is shown to arise from the organic-phase reactions $CeT_3 + R_3NHCl = CeT_3R_3NHCl$, $CeT_3 + R_3NHT = CeT_3R_3NHT$, and $CeT_3 + R_3NHClHT = CeT_3R_3NHClHT$, where T^- represents the enolate ion of HT. It was ascertained that the formation constants for each of these reactions as measured in benzene are the same, and a value was found for log K_s = 4.83 ± 0.15. The synergistic effect in this system was found to be identical in kind and almost in magnitude with that observed in a previous investigation involving americium.

Introduction

The synergistic effect of tri-*n*-octylamine (TNOA or R_3N) on the thenoyltrifluoroacetone (TTA or HT) extractions of thorium(IV),[2] americium(III),[3] cobalt(II), and zinc(II)[4] have been previously examined. In the first two studies, the aqueous phase contained hydrochloric acid and lithium chloride. Under the conditions used in these studies, three amine species were known to exist: R_3NHCl, R_3NHT, and $R_3NHClHT$.[5,6]

The enhancement in the extraction of thorium was attributed to the attachment of R_3NHCl to one of the TTA molecules in the $Th(TTA)_4$ complex. In the americium(III) study, the enhancement was found to be 400 times greater than the effect exhibited in the thorium study. The three amine species were found to contribute equally to this effect and it was believed that they were bonded directly to the metal.

(1) This research performed under the auspices of the United States Atomic Energy Commission.

(2) L. Newman and P. Klotz, *J. Phys. Chem.*, **67**, 205 (1963).

(3) L. Newman and P. Klotz, *Inorg. Chem.*, **5**, 461 (1966).

(4) C. H. Ke and N. C. Li in "Solvent Extraction Research," A. S. Kertes and Y. Marcus, Ed., Wiley, New York, N. Y., 1969, p 281.

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In order to determine if the three amine species behave in the same way with other metals, cerium(III) was chosen to be examined under similar conditions.

Experimental Section

Methods and Apparatus.—The synergistic extraction of cerium-(III) due to the addition of TNOA to a TTA solution in benzene was investigated by using much the same techniques as employed in a previous study of americium(III).[3]

A titration method was again used where the TNOA and TTA concentrations were kept constant in the organic phase (see ref 3 for details). The phase volumes were kept equal throughout each experiment and only the pH was increased by the addition of LiOH. The aqueous phase consisted of tracer levels of the metal ion and known concentrations of HCl, and in all but one experiment the ionic strength was maintained at 2 with LiCl.

This series of experiments was conducted in a stoppered, jacketed beaker whose temperature was maintained at 25.1 ± 0.1°. Mixing of the two phases was accomplished by using a magnetic stirrer in conjunction with a Teflon-coated stirring bar. The pH was monitored by using an Instrumentation Laboratories combined electrode with a Radiometer Model 4 pH meter. Calibration of the glass electrode was accomplished using the known acid concentration in the initial solution. Repetitive pH measurements made during the experiment were found to be reproducible to 0.005 unit with negligible electrode drift.

Distribution coefficients were determined by γ-counting duplicate 1-ml aliquots from the aqueous and organic phases containing ^{144}Ce in a "well type" scintillation counter. The aliquots were counted 1 day after separation in order to permit attainment of the ^{144}Ce–^{144}Pr equilibrium. The activity in the aqueous phase prior to extraction was $\sim 1.2 \times 10^{5}$ counts min^{-1} ml^{-1}. To be certain that these experiments were conducted under equilibrium conditions, reverse titrations were performed and similar experiments run for different periods of time were compared.

In order to preestablish equilibrium conditions in the organic phase, the organic solutions were contacted with an aqueous solution which was identical with that used in the experiment except for the absence of ^{144}Ce. A constant concentration of free TTA was maintained by accounting for the amount consumed through interaction with the amine. The method for doing this has been previously explained.[2]

Reagents.—^{144}Ce–^{144}Pr was obtained from Oak Ridge National Laboratory and was examined both before and after TTA extraction and found to be free of γ-emitting impurities in the 0–1.5-MeV energy range. The purifications of TTA (A. D. MacKay) and TNOA (Eastman Organic) have been previously discussed.[5] Reagent grade benzene (Baker and Adamson) was used as the organic diluent. The LiCl (Baker and Adamson) solutions were filtered before use.

Results

Initial Considerations. TTA and Amine Extraction.

—Before examining the synergistic effect that is caused by TNOA on the TTA extraction of cerium(III), it is first necessary to evaluate the properties of each of the extractants.

The TTA extraction of cerium(III) can be expressed as

$$K_{Ce} = \frac{(CeT_3)(H^+)^3}{(Ce^{3+})(HT)^3} \tag{1}$$

where the charged species are present in the aqueous phase and the uncharged in the organic phase. Since most experiments were conducted in 2 M LiCl, the chloride complexation of cerium has to be considered. The free cerium thus becomes

$$(Ce^{3+}) = \frac{(Ce)_a}{\sum_{0}^{N} \beta_{n,Cl}(Cl^-)^n} \tag{2}$$

where $(Ce)_a$ is the total analytical concentration of cerium in the aqueous phase at equilibrium. The for-
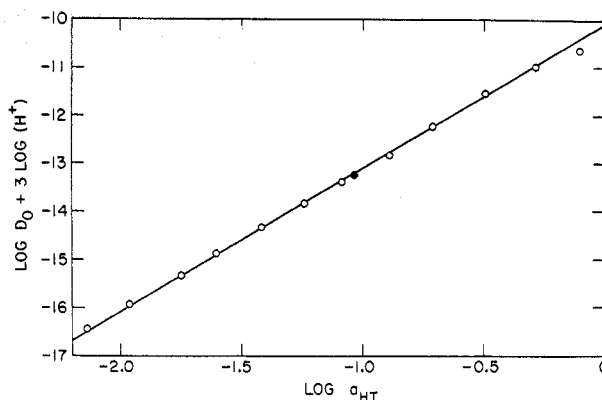

Figure 1.—The distribution of cerium as a function of TTA: O, pH 4.4; ●, average value calculated from 0.1 M TTA at varying pH.

mation constants for the cerium chloride interaction can be written as

$$\beta_{n,Cl} = \frac{(CeCl_n^{3-n})}{(Ce^{3+})(Cl^-)^n} \tag{3}$$

where n can be any value from 0 to N.

Employing the usual definition for the distribution coefficient, the TTA extraction of cerium from an aqueous chloride solution is expressed as

$$D_0 = \frac{(CeT_3)}{(Ce^{3+})\sum_{0}^{N}\beta_{n,Cl}(Cl^-)^n} \tag{4}$$

By substituting eq 1 and defining

$$K^0_{Ce} = K_{Ce}\left[\sum_{0}^{N}\beta_{n,Cl}(Cl^-)^n\right]^{-1} \tag{5}$$

we obtained

$$D_0(H^+)^3 = K^0_{Ce}(HT)^3 \tag{6}$$

or in logarithmic form

$$\log D_0 + 3\log (H^+) = \log K^0_{Ce} + 3\log (HT) \tag{7}$$

The data from a distribution experiment performed at a constant pH of 4.4 and ionic strength of 2.0 with varying TTA concentrations were plotted using log $D_0 + 3 \log (H^+)$ as ordinate and log α_{HT} as abscissa. The activity (α_{HT}) of TTA was determined using the formula of King and Reas.[7] Figure 1 shows the resulting plot which has a slope of 3 as predicted by eq 7. The filled symbol represents the average result calculated from an experiment performed at constant 0.1 M TTA where the pH was varied.

As there is not any noticeable change in the slope of this plot, the presence of a TTA addition compound was not suspected. This contrasts with the result found in the analogous americium study where the formation of an addition compound was clearly indicated.

From the intercept of this plot, the formation constant was determined as

$$\log K^0_{Ce} = -10.10 \pm 0.05 \quad (2\ M\ \text{LiCl})$$

The extraction of cerium(III) by 0.01 M TNOA was examined under the conditions used in this study and

(7) E. L. King and W. H. Reas, *J. Amer. Chem. Soc.*, **73**, 1806 (1951).

the distribution coefficient was found to be $D \leq 10^{-4}$.

Determining the Amine Dependency of the Adduct Formed in the Organic Phase.—The interactions of tri-*n*-octylamine with HCl and TTA have been studied under conditions applicable to this study.[5,6] The measured formation constants are

$$K_{Cl} = \frac{(R_3NHCl)}{(R_3N)(H^+)(Cl^-)} = 1.3 \times 10^4 \qquad (8)$$

$$K_T = \frac{(R_3NHT)}{(R_3N)(HT)} = 1.4 \times 10^3 \qquad (9)$$

$$K_{Cl,T} = \frac{(R_3NHClHT)}{(R_3N)(H^+)(Cl^-)(HT)} = 2.1 \times 10^5 \qquad (10)$$

Assuming that each of these species contributes to the overall synergistic effect by interacting with CeT_3, then the following equilibrium constants have to be considered

$$K_{Ce,Cl} = \frac{(CeT_3R_3NHCl)}{(CeT_3)(R_3NHCl)} \qquad (11)$$

$$K_{Ce,T} = \frac{(CeT_3R_3NHT)}{(CeT_3)(R_3NHT)} \qquad (12)$$

$$K_{Ce,Cl,T} = \frac{(CeT_3R_3NHClHT)}{(CeT_3)(R_3NHClHT)} \qquad (13)$$

As can be readily seen, these constants presuppose a 1:1 interaction between each amine species and CeT_3. Under the conditions used in this study, the fraction of amine existing in the free state never exceeds 0.8% of the total. Therefore, the contribution of the free amine to the synergistic effect was not considered. The distribution coefficient can now be defined as

$$D = \frac{(CeT_3) + (CeT_3R_3NHCl) + (CeT_3R_3NHT) + (CeT_3R_3NHClHT)}{(Ce^{3+})\sum_{0}^{N}\beta_{n,Cl}(Cl^-)^n} \qquad (14)$$

and substituting, we obtain

$$D = D_0 + K^0_{Ce} \times$$
$$\left[\frac{K_{Ce,Cl}K_{Cl}(H^+)(Cl^-) + K_{Ce,T}K_T(HT) + K_{Ce,Cl,T}K_{Cl,T}(H^+)(Cl^-)(HT)}{K_{Cl}(H^+)(Cl^-) + K_T(HT) + K_{Cl,T}(H^+)(Cl^-)(HT)} \right] \times$$
$$\frac{(HT)^3}{(H^+)^3}(R_3N)_T \qquad (15)$$

where $(R_3N)_T$ is the analytical amine concentration.

If the logarithm of $D - D_0$ is plotted as ordinate and the logarithm of $(R_3N)_T$ as abscissa, a straight line having a slope of 1 is predicted by eq 15 under conditions where the pH, free TTA, and chloride are held constant.

The amine dependency was tested by performing a distribution experiment in which the TNOA concentration was varied from $\sim 2 \times 10^{-5}$ to $\sim 2 \times 10^{-2}$ M while the TTA concentration was kept constant at 0.1 M and the pH at 3.79. The log D_0 was determined as -1.74 from two initial points taken prior to the addition of TNOA.

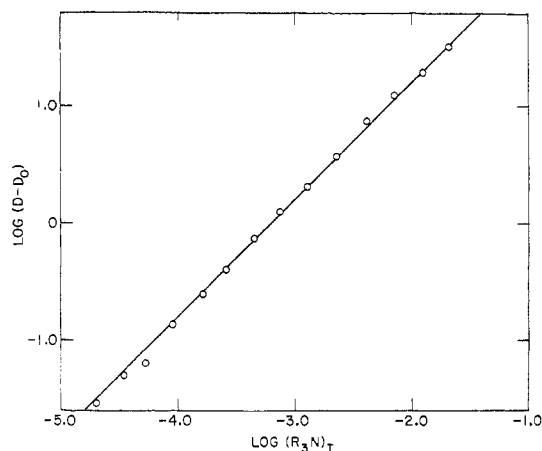Figure 2 shows the resulting plot of the data, through

Figure 2.—Demonstration of the first-power dependency of synergism on amine concentration at 0.1 M TTA and 2.0 M chloride.

which a straight line with a slope of 1 was drawn. This line fits the data very well so the assumption that only one amine per americium is present in the organic phase adduct is substantiated.

Determination of the Synergistic Agent.—It was now necessary to determine which species caused the enhanced extraction and the magnitude of the effect. The experimental approach which was adopted for studying the synergistic effect involved obtaining distribution data at constant TTA and TNOA concentrations while increasing the pH.

Three groups of experiments were performed in an attempt to evaluate the effect of each amine species. The first group of experiments was conducted at 0.1 M TTA for 0 and 10^{-2} M TNOA. During these experiments the pH was varied from 2.5 to 5.5 and the chloride concentration was kept at 2 M. A second set of data was obtained at 0.01 M chloride where the pH was varied from 2.0 to 4.5. The TTA concentration was 0.1 M and the amine concentrations were 0.0 and 10^{-2} M. The final group of experiments was performed at a 1 M TTA concentration and 10^{-2} M amine. Lithium chloride was again used in maintaining the ionic strength at 2 while the pH was varied from 1.5 to 3.5.

In order to know how well we are testing for the effect of each of the amine species in these series of experiments, the fraction of the total TNOA concentration existing in each form was calculated at selected pH levels. These calculations were performed using the

TABLE I
GUIDE FOR THE DISTRIBUTION OF THE AMINE AT REPRESENTATIVE pH VALUES FOR BOTH LEVELS OF TTA[a]

		Fractional distribution			
(HT), M	pH	R_3N	R_3NHCl	R_3NHT	$R_3NHClHT$
0.1	2.5	0.003	0.246	0.385	0.366
	3.5	0.007	0.055	0.857	0.081
	4.5	0.008	0.006	0.977	0.009
1	1.5	0.0001	0.069	0.088	0.843
	2.5	0.0005	0.038	0.492	0.469
	3.5	0.0009	0.007	0.906	0.086
0.1[b]	2.0	0.007	0.009	0.971	0.013
	3.0	0.0077	0.0009	0.990	0.001
	4.0	0.0077	0.0001	0.992	0.0001
0.1	3.8	0.007	0.029	0.920	0.044

[a] Aqueous = 2.0 M LiCl; organic = benzene. [b] Ionic strength of the aqueous phase was 0.01.
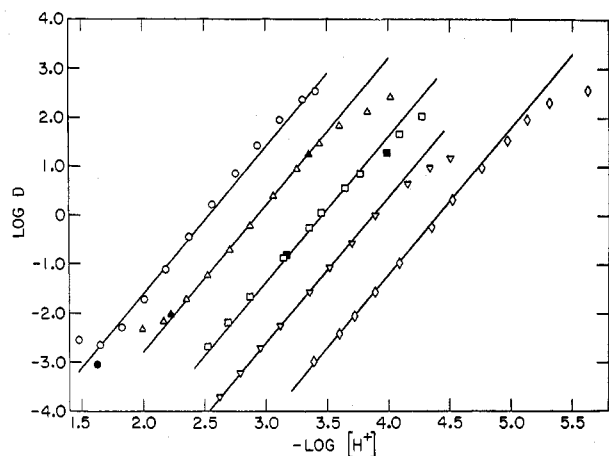
Figure 3.—Distribution data demonstrating the synergistic effect as a function of pH. At 0.1 M TTA and 2.0 M chloride: ◇, no amine; ▢, 10^{-2} M amine. At 1 M TTA and 2.0 M chloride: ○, 10^{-2} M amine. At 0.1 M TTA and 0.01 M chloride: ▽, no amine; △, 10^{-2} M amine. Solid symbols indicate data from a reverse titration.

Figure 4.—Demonstration that the synergistic constants for all the species are the same. Symbols represent the equivalent points as in Figure 3.

formation constants given in eq 8–10. The results are given in Table I.

An examination of this table shows that the effects of both R_3NHT and $R_3NHClHT$ have been thoroughly tested since they have existed both as major and minor components during the series of experiments. R_3N-HCl was not tested as completely as desired due to the relatively high pH necessary for the TTA extraction of cerium(III). However, 24.6% of the amine is in the hydrochloride form during part of these experiments and at this level its effect should be noticeable.

The data from this series of experiments were plotted using log D as the ordinate and $-$log (H^+) as the abscissa. The resulting plots are shown in Figure 3. Several similarities are apparent between these data and those obtained in the americium(III) study. However, the most important similarity is that the presence of different ratios of the three amine species simply results in a positive linear displacement of the distribution coefficient. When the data from the TTA extraction of cerium(III) in the absence of amine are plotted in this way, eq 7 predicts that a straight line with a slope of 3 should result. At the same time, it would be expected that the changing predominance of each amine species should result in changes in slope (see eq 15).

From Figure 3 it can be seen that the data follow this slope quite consistently until they reach the higher distributions where a leveling effect occurs. An effect such as this could be caused by mutual solubilities of the phases or trace impurities.

The filled symbols in Figure 3 indicate "back-titration" points and are a good indication that equilibrium had been established throughout the experiment. These data points were obtained as follows. After the desired pH range was examined, hydrochloric acid was added to the aqueous phase and the system was reequilibrated. Had equilibrium not been reached, then the distribution coefficients determined for the back-titration points would not have been consistent with the earlier data.

After examining the effects of the three amine species present in the organic phase, the most significant ob-
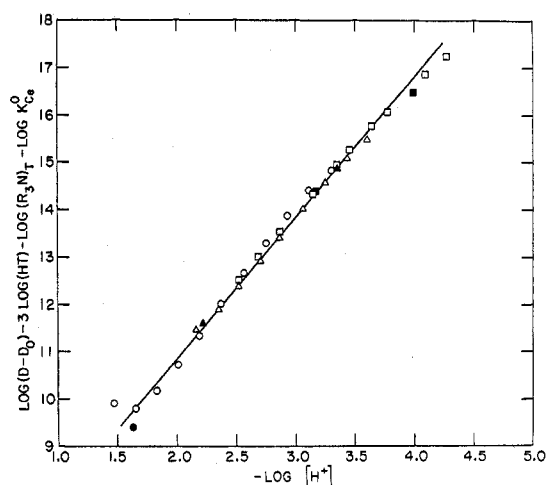
servation is that each species increases the TTA extraction of cerium(III) to the same extent. This effect is identical with that observed in the extraction of americium.

Since each amine species appears to cause the synergistic effect to the same degree, the constants $K_{Ce,Cl}$, $K_{Ce,T}$, and $K_{Ce,Cl,T}$ should be able to be replaced by a single constant K_s in which case eq 15 becomes

$$\log \frac{(D - D_0)}{(HT)^3(R_3N)_T(K^0_{Ce})} = \log K_s - 3 \log (H^+) \quad (16)$$

which is in a form that predicts a synergistic effect independent of the amine species.

The data from all experiments should thereby be capable of incorporation into one graph by plotting the left-hand side of eq 16 $vs.$ $-$log (H^+). If K_s is a constant, then the data should merge into a straight line which has a slope of 3 and an intercept equal to log K_s.

The value of log K^0_{Ce} from the 2 M lithium chloride data was previously determined as -10.10. The analogous constant for the extraction from 0.01 M chloride was calculated from each data point as log K^0_{Ce} = -8.52. At any given acidity in these experiments D is nearly three orders of magnitude larger than D_0 so in these calculations $D \approx D - D_0$.

Figure 4 shows the resulting plot when the data are plotted in this manner. The data indeed coalesce into one curve. A straight line with a slope of 3 was put through the data and appears to fit quite well. There is a very slight negative bias at high pH values which probably arises from the high distributions involved.

In the final calculation for the synergistic formation constant, extreme values of pH were neglected and the position of the straight line shown in Figure 4 was obtained by averaging the values of K_s calculated for each data point. The value obtained is log K_s = 4.83 ± 0.15. The value obtained for americium was 5.03.

Discussion

The synergistic effect of tri-n-octylamine on the solvent extraction of cerium by thenoyltrifluoroacetone is identical in kind with that of americium and almost identical in magnitude. Of course this is not to say that we would predict that all elements would exhibit

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.

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

BY ROBERT BUCHACEK AND GILBERT GORDON*

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 $U(IV) + Cl(III) + phenol \rightarrow U(VI) + H^+ + chlorophenols$. 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}, $K_2 = 4.1_3 \pm 0.2_5$ 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.
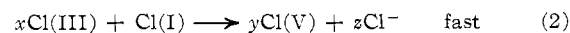
Introduction

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.
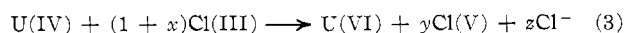
The present study was initiated in an attempt to understand better those factors which influence reactivity patterns of the chlorine oxidants with metal ions. In this study the oxidation of uranium(IV) by chlorine-(III) affords the possibility of either two successive one-electron transfers or one two-electron 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

$$U(IV) + Cl(III) \longrightarrow U(VI) + Cl(I) \quad slow \quad (1)$$

$$xCl(III) + Cl(I) \longrightarrow yCl(V) + zCl^- \quad fast \quad (2)$$

to give

$$U(IV) + (1 + x)Cl(III) \longrightarrow U(VI) + yCl(V) + zCl^- \quad (3)$$

as the overall stoichiometry. Reaction 1 is rate deter-

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