

Studies on Metal Carbonate Equilibria. 4. Reduction of the Tris(carbonato)dioxouranate(VI) Ion, $\text{UO}_2(\text{CO}_3)_3^{4-}$, in Hydrogen Carbonate Solutions

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The redox equilibria between U(VI) and U(IV) have been studied at 25 °C in 3 M NaClO_4 by measuring the potential of inert mercury electrodes against a hydrogen half-cell as well as the light absorbance at 660 nm. The test solutions were equilibrated with $\text{CO}_2\text{-N}_2$ mixtures of known composition. The total uranium concentrations ranged between 10^{-3} and 10^{-2} M, the acidity between 10^{-9} and 10^{-8} M, and the partial pressure of CO_2 from 0.02 to 0.1 atm. The potentiometric and spectrophotometric data have been explained by assuming the equilibrium $\text{UO}_2(\text{CO}_3)_3^{4-} + 2e^- + 2\text{CO}_2(\text{g}) \rightleftharpoons \text{U}(\text{CO}_3)_5^{6-}$ ($E^\circ = -0.279 \pm 0.001$ V). Spectrophotometric evidence for the formation of U(V) has also been obtained.

Introduction

Carbonate and hydroxide are two of the most important ligands in most groundwaters. They form very stable soluble complexes with actinoid elements in their various oxidation states. A number of solid actinoid compounds containing hydroxide and carbonate have also been described. Environmental effects of actinoids are a problem of great concern in connection with the implementation of nuclear waste repositories. All modeling of nuclear waste-water interactions and the subsequent migration of actinoids in groundwater requires a thorough understanding of their solution chemistry.¹ The chemistry of uranium in groundwater has for many decades been of interest for geochemists when discussing the mechanism of uranium ore formation, e.g. sandstone type and "roll-front" deposits.^{2,3} The U(VI)- CO_3^{2-} - H_2O system is fairly well-known; some aspects have been described in parts 1⁴ and 2⁵ of this series. The situation is different for the U(V)- and U(IV)- CO_3^{2-} - H_2O systems about which very little quantitative thermodynamic information is available.

Th(IV) and Ce(IV) have been reported to form solid carbonate compounds of the composition $\text{Na}_6\text{M}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$. Recently, their structures have been determined by X-ray diffraction.^{6,7} The solid phases contain discrete pentakis(carbonato) complexes with all ligands bonded in a bidentate fashion. The coordination polyhedron formed by the ten coordinated oxygens is severely distorted from all the possible ideal geometries for ten-coordination. A solid with the same composition as that of the thorium compound is also formed by uranium(IV).⁸ In view of the similarities in size and chemical properties of U(IV) and Th(IV), it is very probable that the two compounds are isostructural.

McClaine et al.⁸ have made an excellent pioneering study on the carbonate chemistry of uranium in oxidation states +4, +5, and +6. Their study describes rather well the conditions under which the carbonate complexes are formed. Wester and Sullivan⁹ have given additional evidence for the formation of soluble carbonate complexes of U(IV) and U(V). However, the only quantitative information about the stability constants of actinoid(IV) carbonate complexes is the value $\log \beta = 47$ for the formation of PuCO_3^{2+} given by Moskvina and Gel'man.¹⁰ The authors have not taken proper account of the hydrolysis of Pu(IV) when interpreting their experimental data, and the constant is very likely in error by many orders of magnitude.

This paper deals with the chemistry of uranium(IV) in carbonate solutions in the acidity range 10^{-8} – 10^{-9} M. The aim of the study is to obtain quantitative information of the stoichiometry and the stability constants of the species formed

in the uranium(IV) carbonate-water system under the experimental conditions studied. We are also interested in the normal potential of U(VI)/U(IV) in carbonate solutions.

Notations

a	= partial pressure of CO_2
A_λ	= absorbance referred to 1-cm optical path length
B	= total concentration of uranium
h	= concentration of H^+
d	= concentration of HCO_3^-
H	= $[\text{ClO}_4^-] - [\text{Na}^+] - 2B$ = analytical concentration excess of H^+
w	= moles of electrons removed by anodical oxidation
θ	= analytical concentration excess of electrons, referred to U(VI) as zero level
x	= concentration of electrons (defined by eq 2)
Z	= θ/B = average number of electrons per uranium atom
$K_{6,i}$	= conditional equilibrium constant for $p\text{U(VI)} + (6p - i)e^- \rightleftharpoons \text{U}_p(i)$
$\beta_{q,r}$	= equilibrium constant for $\text{UO}_2(\text{CO}_3)_6^{4-} + 2e^- + (7 + r - q)\text{CO}_2(\text{g}) + 5\text{H}_2\text{O} \rightleftharpoons \text{U}(\text{OH})_q(\text{CO}_2)_r^{4-q} + (10 - q)\text{HCO}_3^-$
ϵ	= molar absorption coefficient at 660 nm
$(\text{OH})\text{CO}_2^- \rightleftharpoons \text{HCO}_3^-$	
$(\text{OH})_2\text{CO}_2^- \rightleftharpoons \text{CO}_3^{2-}$	

Method

The study of the uranium redox equilibria was made in hydrogen carbonate solutions equilibrated with $\text{CO}_2\text{-N}_2$ mixtures of known partial pressure, a , of CO_2 . The solutions contained U(VI) and varying amounts of uranium in lower oxidation states. The relative amounts of the various oxidation states were varied coulometrically. The redox potential was measured at 25 °C in 3 M NaClO_4 with mercury as the inert electrode. In addition, the light absorption, A_λ , at 660 nm was measured.

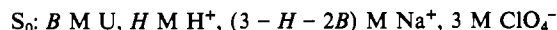
The experiments were made as titrations where in each series the total uranium concentration, B , the proton concentration, h , and the partial pressure, a , of CO_2 in equilibrium with the test solution were kept constant, whereas the analytical excess of electrons, θ , was varied by constant-current coulometry. The values of B , h , and a were in

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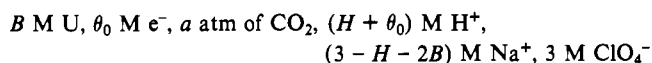
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the ranges $1 \times 10^{-3} < B < 1 \times 10^{-2}$ M, $10^{-9} < h < 10^{-8}$ M, and $0.02 < a < 0.1$ atm. These limits were imposed by the following: (1) There is formation of a whitish precipitate that rapidly turns black (possibly UO_2) at high h and high values of B and a . (2) At low values of B the redox potential is unreliable because of the low redox-buffer capacity of the solution. Errors caused by oxidizing impurities also increase with decreasing B . (3) The time to attain equilibrium is very long at low values of a . (4) The solubility of NaHCO_3 in 3 M NaClO_4 is also limiting the h range that can be studied.

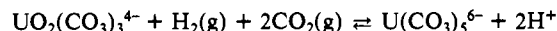
The main experimental obstacle was the extreme ease with which solutions of uranium in lower oxidation states were oxidized by air. This problem was solved by a procedure in which the test solutions were reduced in situ. A known volume, V_0 , of a solution with the composition



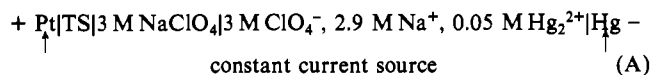
was introduced in the titration vessel. The initial U(VI) was reduced by H_2 with use of Pd deposited on a Pt net as a catalyst. A 90–95% reduction was obtained overnight. After the reduction, the net could be lifted out of the solution without opening the titration vessel. The hydrogen was then replaced by bubbling a CO_2 - N_2 mixture through the solution, which after reduction had the composition



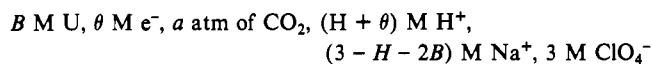
($H + \theta_0$) is the total concentration of hydrogen ions after the reduction of U(VI) with H_2 . The increase θ_0 is due to the reaction



All quantities except θ_0 are known. To determine θ_0 , a known volume was taken under a nonoxidizing atmosphere into a buret. The device used is similar to that described by Biedermann and Ciavatta.¹¹ In order to reduce errors due to the possible oxidation of the solution, only the central portion in the buret was used. This was added to a known volume of standardized KMnO_4 , the excess of which was titrated iodometrically. The composition of the remaining volume, V , of the solution was varied by stepwise coulometric oxidation, i.e. by decreasing the analytical concentration excess of electrons θ . The oxidation was performed by using the coulometric circuit



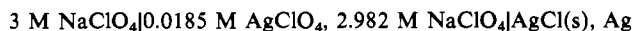
The test solution, TS, has the composition



where $\theta = \theta_0 - w/V$, after passing w faradays through the cell. The electrolysis was carried out at lower current densities than 3×10^{-5} A/cm² in order to ensure 100% current efficiency. The current efficiency was checked by measuring the redox potential after repeated cycles of oxidation and reduction. The emf always coincided within a few hundredths of 1 mV, indicating a current efficiency close to theoretical. This result was confirmed by interrupting a few of the titrations and analyzing the solutions by the titrimetric procedure previously described. The coulometric and titrimetric values of θ always agreed within 0.5%, or better. The emf E_B and E_C of the following cells were measured after each oxidation step in the titration



GE denotes a glass electrode and RE the reference half-cell



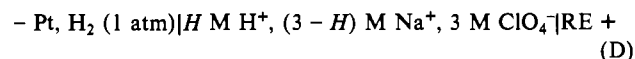
The experimental arrangement also allowed the absorbance A_λ at 660 nm to be measured at each step in the titration. Absorbancy data were recorded in most of the titrations.

The emf of cell C is equal to

$$E_C = E^\circ_C - 0.05916 \log H + E_j$$

where E°_C is a constant and E_j the liquid-junction potential arising between TS and 3 M NaClO_4 . In a previous study,⁴ we have found that $E_j = 7.2 \times 10^{-3}(H + 2B)$ V. The value of E_C is constant within a few tenths of 1 mV throughout the titration. This is due to the fairly large buffer capacity of the solutions studied. The nearly constant value of h simplifies the treatment of the data.

In order to relate the emf of cell B to the normal hydrogen electrode, the emf, E_D , of the cell



was measured

$$E_D = E^\circ_D - 0.05916 \log H - 0.0169H$$

where the last term is the liquid-junction potential determined elsewhere.¹² E°_D was evaluated in a series of measurements and is equal to $0.67280 \pm 4 \times 10^{-5}$ V. The potential, E , referred to the normal hydrogen electrode can now be calculated:

$$E = E^\circ_D - E_B + E_j \quad (1)$$

From the experimental data E , A_λ , B , and θ the quantities $Z = \theta/B$ and $\log(A_\lambda/B)$ are calculated as functions of $\log x$, with

$$\log x = -E/0.05916 \quad (2)$$

The data sets $Z = f(\log x)$ and $\log(A_\lambda/B) = g(\log x)$ form the basis for the mathematical analysis of the data. These data are given in Table I.

Experimental Section

Reagents and Analysis. Uranium(VI) perchlorate, perchloric acid, sodium hydrogen carbonate, sodium perchlorate, and silver perchlorate solutions were prepared as described in a previous paper⁴ of this series. The preparation of mercury perchlorate solutions has been described elsewhere.¹³

The Pd catalyst was obtained by cathodic reduction of a 1% Pd-(II)-1 M HCl solution on a Pt net. The current was ~ 0.3 A. H_2 as well as N_2 - CO_2 gas mixtures were purified and made free of oxygen by passing them through a series of washing bottles containing, in the following order, 1 M H_2SO_4 , H_2O , and a Cr(II) solution on Zn(Hg). The gas was finally bubbled through 3 M NaClO_4 to obtain the correct water vapor pressure.

Measurements. All the emf measurements were performed in a paraffin oil bath at 25.00 ± 0.02 °C. The bath and the measuring equipment were placed in a thermostat room kept at 25.0 ± 0.2 °C. The atmospheric pressure was recorded by means of a Kistler Z 10588 piezoresistive pressure transducer with a precision of 5×10^{-4} atm. The cell arrangement was similar to that described by Forsling et al.¹⁴ The Ag/AgCl electrodes were prepared according to Brown.¹⁵ Metrohm EA 109 glass electrodes were used. A comparison with a hydrogen electrode showed that they have a negligible alkali error in the pH range studied in this work. The inert electrodes consisted of two 5 N mercury pools at the bottom of the test vessel. The experiments were made as titrations, where stepwise oxidation/reductions were made by using the coulometric circuit (C). The constant-current source was an Electronic Measurement C 633B power supply. The absorption at λ 660 nm was measured in Helma 10-cm cylindrical quartz cuvettes by using a Cary 219 spectrophotometer. A 3 M NaClO_4 solution was used as the reference. The estimated error in A_λ was 5×10^{-4} . The whole absorption spectrum between 350 and 750 nm was recorded, but only the value of A_λ at 660 nm was used in the calculations. A constant value of A_λ was usually obtained within 30–40 min after the electrolysis had been stopped. The test solution was circulated between the titration vessel and the cuvette by means of an all-glass piston pump. The pump was stopped during the measurement of the emf values. These were measured with a precision of 0.02 mV by using a Fluke 8810 digital voltmeter. In order to be able to measure the potential of the glass electrode cell, E_C , a preamplifier (Analog Devices 309K) had to be used. The emf values became constant within 2–3 h. A more rapid equilibrium value

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Table I. Experimental Data ($Z, \log x, \log (A_\lambda B^{-1})_{B,a,d}^a$)

$B = 2.981 \times 10^{-3} \text{ M}, -\log a = 1.012 \pm 0.003, -\log d = 0.897$

($Z, \log x, \log (A_\lambda B^{-1})$)
(1.865, 6.337, 1.291), (1.763, 6.191, 1.266), (1.560, 6.040, 1.210), (1.458, 5.974, 1.180), (1.356, 5.913, 1.147), (1.252, 5.863, 1.111), (1.151, 5.828, 1.071), (1.050, 5.775, 1.028), (0.948, 5.724, 0.981), (0.846, 5.676, 0.928), (0.744, 5.619, 0.868), (0.642, 5.570, 0.798), (0.540, 5.516, 0.715), (0.438, 5.455, 0.615), (0.336, 5.384, 0.485), (0.234, 5.310, 0.295)

$B = 3.011 \times 10^{-3} \text{ M}, -\log a = 1.007 \pm 0.001, -\log d = 0.603$

($Z, \log x, \log (A_\lambda B^{-1})$)
(1.866, 6.271, 1.258), (1.763, 6.131, 1.232), (1.654, 6.050, 1.208), (1.543, 6.001, 1.176), (1.434, 5.921, 1.144), (1.324, 5.864, 1.111), (1.215, 5.816, 1.076), (1.105, 5.788, 1.036), (0.997, 5.742, 0.993), (0.892, 5.676, 0.945), (0.784, 5.630, 0.891), (0.675, 5.579, 0.832), (0.564, 5.528, 0.758), (0.460, 5.481, 0.672), (0.354, 5.404, 0.564), (0.249, 5.322, 0.416), (0.150, 5.193, 0.200)

$B = 2.998 \times 10^{-3} \text{ M}, -\log a = 1.009 \pm 0.002, -\log d = 0.573$

($Z, \log x, \log (A_\lambda B^{-1})$)
(1.814, 6.227, 1.255), (1.706, 6.088, 1.229), (1.600, 6.012, 1.202), (1.494, 5.947, 1.174), (1.388, 5.898, 1.142), (1.283, 5.851, 1.108), (1.177, 5.801, 1.071), (1.072, 5.756, 1.031), (0.967, 5.709, 0.986), (0.861, 5.664, 0.936), (0.755, 5.617, 0.883), (0.649, 5.567, 0.818), (0.543, 5.511, 0.743), (0.438, 5.446, 0.654), (0.332, 5.370, 0.538), (0.226, 5.270, 0.376), (0.121, 5.114, 0.124), (0.098, 5.070, 0.051), (0.076, 5.016, . . .), (0.032, 4.832, . . .)

$B = 10.070 \times 10^{-3} \text{ M}, -\log a = 1.002 \pm 0.004, -\log d = 0.627$

($Z, \log x$)
(0.154, 5.197), (0.210, 5.273), (0.266, 5.327), (0.322, 5.376), (0.378, 5.421), (0.434, 5.450), (0.492, 5.482), (0.576, 5.530), (0.662, 5.571), (0.746, 5.605), (0.832, 5.640), (0.916, 5.672), (1.001, 5.702)

$B = 2.998 \times 10^{-3} \text{ M}, -\log a = 1.323 \pm 0.001, -\log d = 0.669$

($Z, \log x, \log (A_\lambda B^{-1})$)
(1.808, 6.503, 1.215), (1.709, 6.413, 1.193), (1.613, 6.345, 1.170), (1.430, 6.236, 1.118), (1.249, 6.147, 1.059), (1.066, 6.066, 0.990), (0.885, 5.984, 0.909), (0.698, 5.909, 0.809), (0.515, 5.807, 0.677), (0.335, 5.684, 0.448), (0.152, 5.498, 0.144), (0.056, 5.287, -0.262)

^a For each series, an average partial pressure of CO_2 and its maximum deviation are given.

of E_B was obtained in the range $0.7 < Z < 1.3$. We believe that the slow equilibria are due both to the equilibration between solution and gas phase and to the slow electrode kinetics in the U(VI)/U(IV) system. As previously suggested,⁸ it is probable that the actual electrode reaction is a one-electron process involving U(V) whose concentration is largest at $Z = 1$. The tedious and time-consuming titrations could, however, be carried out by using a computer-controlled system, based on a Commodore 3032 (PET) microcomputer and described elsewhere.¹⁶

Treatment of the Experimental Data

The composition and the equilibrium constants of the carbonate complexes were determined from the $Z(\log x)$ data by using a two-stage procedure. In the first stage the oxidation number and the number of uranium atoms in the complexes were determined from titrations at constant a and h . The small variations in a , due to changes in the atmospheric pressure, and the variations in h can be neglected at this stage. In the second stage, the numbers of carbonate (or the numbers of OH^- and CO_2) groups in the complexes were determined by comparing titrations at different h and a levels.

As a consistency test, the $\log (A_\lambda/B)(\log x)$ data were compared with the results obtained from the $Z(\log x)$ functions.

Evaluation of the Oxidation Number and the Nuclearity. The complexes formed may be written $\text{U}_p(\text{OH})_q(\text{CO}_2)_r$, which at

$B = 1.012 \times 10^{-3} \text{ M}, -\log a = 1.317 \pm 0.006, -\log d = 0.634$

($Z, \log x$)
(1.813, 6.524), (1.719, 6.460), (1.533, 6.317), (1.346, 6.219), (1.161, 6.136), (0.974, 6.051), (0.788, 5.966), (0.602, 5.873), (0.415, 5.759), (0.229, 5.613)

$B = 2.981 \times 10^{-3} \text{ M}, -\log a = 1.765 \pm 0.004, -\log d = 1.013$

($Z, \log x, \log (A_\lambda B^{-1})$)
(1.857, 7.030, 1.234), (1.745, 6.903, 1.206), (1.636, 6.806, 1.177), (1.523, 6.738, 1.145), (1.415, 6.673, 1.112), (1.301, 6.627, 1.075), (1.188, 6.565, 1.035), (1.076, 6.513, 0.989), (0.964, 6.462, 0.939), (0.852, 6.408, 0.881), (0.740, 6.355, 0.815), (0.629, 6.293, 0.736), (0.517, 6.240, 0.652), (0.404, 6.162, 0.514), (0.292, 6.067, 0.323), (0.180, 5.949, . . .), (0.137, 5.881, . . .), (0.094, 5.830, . . .)

$B = 3.011 \times 10^{-3} \text{ M}, -\log a = 1.751 \pm 0.001, -\log d = 0.735$

($Z, \log x, \log (A_\lambda B^{-1})$)
(1.881, 7.067, 1.244), (1.771, 6.930, 1.218), (1.663, 6.830, 1.190), (1.556, 6.753, 1.159), (1.448, 6.688, 1.129), (1.342, 6.631, 1.096), (1.236, 6.580, 1.059), (1.128, 6.531, 1.020), (1.023, 6.482, 0.978), (0.916, 6.435, 0.928), (0.811, 6.386, 0.874), (0.705, 6.336, 0.811), (0.602, 6.282, 0.738), (0.501, 6.218, 0.651), (0.382, 6.156, 0.545), (0.280, 6.063, 0.404), (0.174, 5.937, 0.201)

$B = 2.998 \times 10^{-3} \text{ M}, -\log a = 1.723 \pm 0.005, -\log d = 0.712$

($Z, \log x, \log (A_\lambda B^{-1})$)
(1.860, 7.008, 1.226), (1.744, 6.868, 1.198), (1.563, 6.727, 1.151), (1.382, 6.617, 1.099), (1.199, 6.533, 1.037), (1.021, 6.449, 0.966), (0.841, 6.368, 0.881), (0.661, 6.286, 0.778), (0.481, 6.189, 0.638), (0.303, 6.057, 0.432), (0.123, 5.837, 0.024)

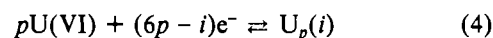
$B = 1.012 \times 10^{-3} \text{ M}, -\log a = 1.718 \pm 0.001, -\log d = 0.712$

($Z, \log x$)
(1.737, 6.865), (1.493, 6.688), (1.249, 6.567), (1.004, 6.457), (0.760, 6.345), (0.516, 6.209), (0.332, 6.077)

constant a and h may be replaced with $U_p(i)$, uranium species with formal charge $i/p < 6+$. Z is then equal to

$$Z = \frac{\sum(6p-i)[U_p(i)]}{[U(\text{VI})] + \sum p[U_p(i)]} \quad (3)$$

The conditional equilibrium constant for



is denoted $K_{6,i}$. Introduction of (2) and $K_{6,i}$ into (3) gives

$$Z = \frac{\sum(6p-i)K_{6,i}[U(\text{VI})]^{p-1}x^{6p-i}}{1 + \sum pK_{6,i}[U(\text{VI})]^{p-1}x^{6p-i}} \quad (5)$$

The $Z(\log x)_{a,h}$ falls on a single curve; i.e., they are independent of B ; hence, mononuclear complexes ($p = 1$) are predominant in the B range investigated. Both the functional dependence of $Z(\log x)$, which indicates that $Z \rightarrow 2$ as $\log x \rightarrow \infty$, and the spectra of the solutions suggest⁹ that the lowest value of i is 4+.

In order to determine $K_{6,i}$ and to decide whether appreciable amounts of U(V) are formed in our solutions or not, we compared the $Z(\log x)_{a,h}$ data with normalized model curves $Y(\log u)$

$$Y = \frac{Lu + 2u^2}{1 + Lu + u^2} \quad (6)$$

$$\log u = \log x + \frac{1}{2} \log K_{6,4} \quad (7)$$

(16) Cachet, J. M.; Wallin, T.; Zeising, J. "A Microcomputer Controlled System for Chemical Measurements", Report TRITA-OKK-2013; Stockholm, 1980.

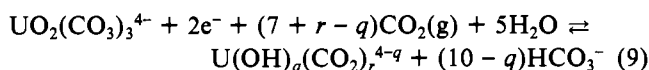
where

$$L = K_{6,5}K_{6,4}^{-1/2} \quad (8)$$

For each set of $Z(\log x)_{a,h}$ data, the best agreement was found with the curve with $L = 0$. Hence, the concentration of U(V) species can be neglected in the concentration range investigated. However, there are experimental observations that strongly indicate that uranium(V) is present in small amounts. This evidence is presented in the Discussion.

The values of $K_{6,4}$ given in Table II are determined from the position of best fit between the theoretical $Y(\log u)$ curve and the experimental $Z(\log x)_{a,h}$ data. The uncertainties are estimated from the limiting positions still giving an acceptable fit.

Evaluation of the Number of CO₂ and OH⁻ Groups in U-(OH)_q(CO₂)_r^{4-q}. The analysis in the previous section indicates that only mononuclear uranium complexes are formed. Hence, all equilibria may be written in the general form



with the equilibrium constant

$$\beta_{q,r} = \frac{[\text{U}(\text{OH})_q(\text{CO}_2)_r]d^{10-q}}{bx^2a^{7+r-q}} \quad (10)$$

b and d stand for $[\text{UO}_2(\text{CO}_3)_3^{4-}]$ and $[\text{HCO}_3^-]$, respectively. Charges have been omitted for brevity.

The functional relation between $\beta_{q,r}$ and the conditional equilibrium constant $K_{6,4}$ is

$$K_{6,4} = \sum \beta_{q,r}a^{7+r-q}/d^{10-q} \quad (11)$$

From the results in Table II, it is evident that $K_{6,4}$ is nearly independent of d at constant a . Hence, the coefficient $(10 - q)$ in (9) is zero; i.e., $q = 10$.

A plot $K_{6,4}$ vs. a is best described by a straight line with the slope 2. This indicates that a single uranium species with $r = 5$ is predominant in the solutions studied. From the intercept, a value of $\beta_{10,5}$ for the formation of $\text{U}(\text{OH})_{10}(\text{CO}_2)_5^{6-}$ ($\equiv \text{U}(\text{CO}_3)_5^{6-}$) was obtained. This value was refined by calculating $\beta_{10,5}$ for each experimental point with the relation

$$\log \frac{Z}{2 - Z} - 2 \log x - 2 \log a = \log \beta_{10,5} \quad (12)$$

The average value of $\log \beta_{10,5}$ calculated from (12) with its standard deviation is given in Table III.

The agreement between the whole set of experimental data and the curve calculated by assuming the redox equilibrium



with $\log \beta_{10,5} = -9.44$ is shown in Figure 1.

From the definition of E

$$E = E^\circ + 0.02958 \log \frac{[\text{UO}_2(\text{CO}_3)_3^{4-}]a^2}{[\text{U}(\text{CO}_3)_5^{6-}]}$$

it follows that the standard potential in 3 M NaClO₄ is equal to

$$E^\circ = 0.02958 \log \beta_{10,5} = -0.279 \pm 0.001 \text{ V}$$

Interpretation of the Spectrophotometric Data. The reproducibility of the redox potential data was very good; nevertheless, we felt that a test was needed to prove that the Z values were not affected by errors due to oxygen contamination or nonquantitative electrodic processes during the electrolysis. This test was made by using the function $\log (A_\lambda/B)(\log x)$. At $\lambda = 660$ nm, the absorption of U(VI) is negligible, while that of U(IV) is close to an absorption maximum.

Table II. Survey of the $K_{6,4}$ Values^a

$-\log a$	$-\log K_{6,4}$	$-\log d$
1.012 ± 0.003	11.49 ± 0.03	0.897
1.007 ± 0.001	11.45 ± 0.03	0.603
1.009 ± 0.002	11.44 ± 0.03	0.573
1.002 ± 0.004	11.44 ± 0.03	0.627
1.323 ± 0.001	12.07 ± 0.03	0.669
1.317 ± 0.006	12.11 ± 0.03	0.634
1.765 ± 0.004	12.95 ± 0.03	1.013
1.751 ± 0.001	12.94 ± 0.03	0.735
1.723 ± 0.005	12.88 ± 0.03	0.712
1.718 ± 0.001	12.90 ± 0.03	0.712

^a Units: a , atm; $K_{6,4}$, M⁻²; d , M.

Table III. Survey of the Final Results of $\beta_{10,5}$ (M⁻² atm⁻²), E° (V), and ϵ (cm⁻¹ M⁻¹)

$-\log \beta_{10,5}$	$-E^\circ$	$\log \epsilon$
9.44 ± 0.03	0.279 ± 0.001	1.29 ± 0.02

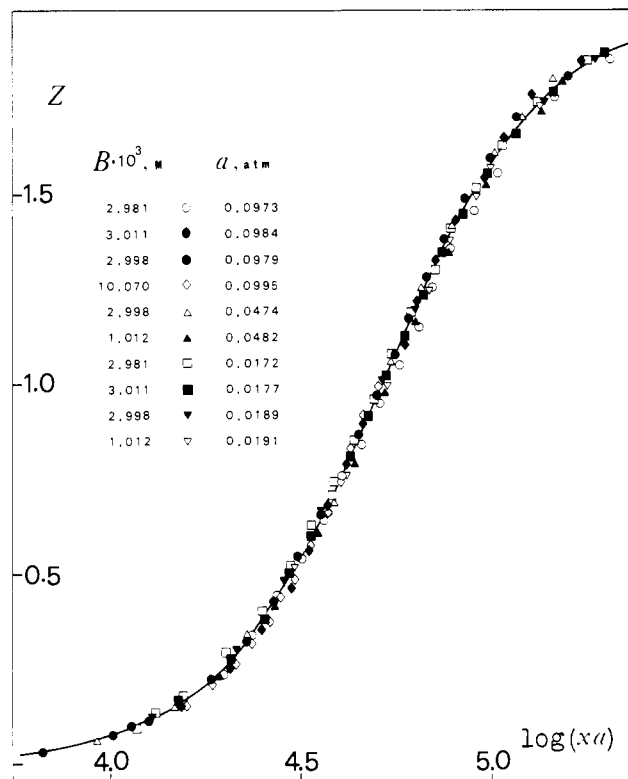


Figure 1. $Z(\log(xa))$ data. The curve has been calculated by assuming $\log \beta_{10,5} = -9.44$.

For a path length of 1 cm, we may under these conditions deduce eq 14. The experimental data, plotted in Figure 2 as

$$\log \frac{A_\lambda}{B} = \log \epsilon + \log \frac{\beta_{10,5}a^2x^2}{1 + \beta_{10,5}a^2x^2} \quad (14)$$

$\log (A_\lambda/B)$ vs. $\log(xa)$, fall on a single curve within the experimental errors. The theoretical curve is calculated by introducing, in the right-hand terms of eq 14, the constants given in Table III. The good agreement between the data and the theoretical model is a satisfactory consistency proof.

Discussion

Possible Formation of Uranium(V) Species. Reduction of $\text{UO}_2(\text{CO}_3)_3^{4-}$ at $8 < -\log h < 9$ leads to the formation of $\text{U}(\text{CO}_3)_5^{6-}$ as the predominant species. Even though no quantitative evidence for the formation of uranium(V) species could be obtained, there are some qualitative observations to support its formation in small amounts.

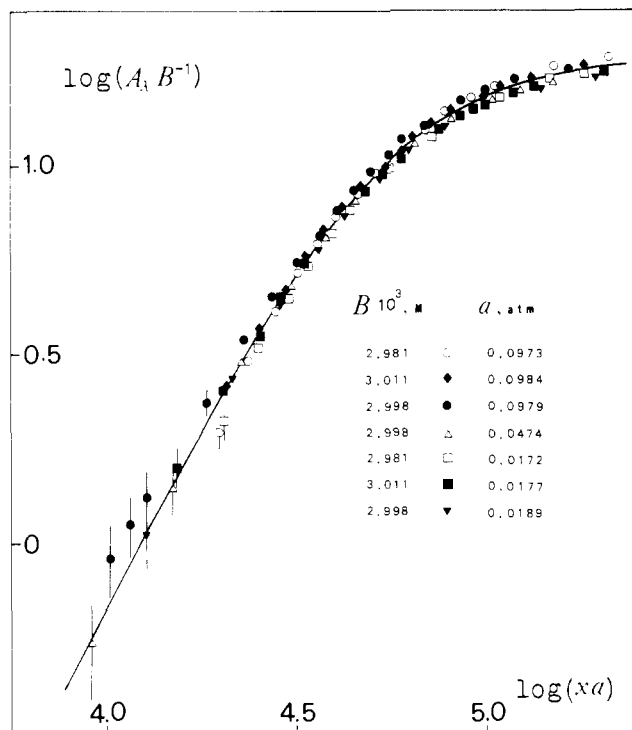


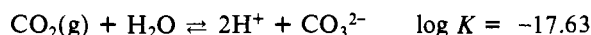
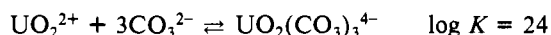
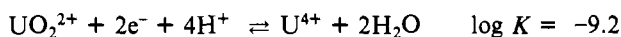
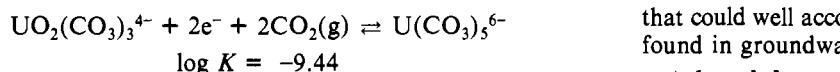
Figure 2. $\log(A_i B^{-1})$ vs $\log(xa)$ data. The curve has been calculated with $\log \beta_{10,5} = -9.44$ and $\log \epsilon = 1.29$. The uncertainty of the experimental points corresponds to an estimated error of 5×10^{-4} in the measurement of the absorbance.

The most direct evidence is obtained from the spectrophotometric measurements. The value of the hydrogen ion concentration in the test solution after reduction of U(VI) to U(IV) is close to 10^{-10} M. The spectrum of this solution is similar to that reported by Wester and Sullivan.⁹ There are small but significant changes in this spectrum when the solution has been saturated with the CO_2 - N_2 mixture. The absorption at 660 nm, where only U(IV) absorbs, increases by a few percent. A similar increase is obtained at 438 nm, where the largest part of the absorption is due to U(VI). The only possible explanation to this change is a reaction of the type



where the formation of uranium(V) is favored by low h in accordance with observations by other authors.^{8,9} A quantitative study of the redox properties of uranium in carbonate solutions at lower h is under way.

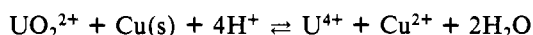
By combination of the constants for the reactions



one obtains an estimate of the equilibrium constant β_5 for the reaction

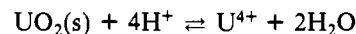


The main uncertainty in this constant is determined by the uncertainties of the standard potential of the $\text{UO}_2^{2+}/\text{U}^{4+}$ couple and the equilibrium constant for the formation of $\text{UO}_2(\text{CO}_3)_3^{4-}$. On the basis of some preliminary experiments on the equilibrium



we have selected the value 0.273 ± 0.005 V, proposed by Fuger and Oetting,¹⁷ even though a fairly large number of authors indicate a value in the range 0.32–0.33 V. An experimental redetermination of the standard potential for $\text{UO}_2^{2+}/\text{U}^{4+}$ is under way in our laboratory. The equilibrium constant for the third reaction is based on the results of a previous work⁴ and preliminary measurements of the solubility product of UO_2CO_3 , to be reported shortly. The magnitude of $\log \beta_5$ does not explain the fairly high concentration of U(IV), which can be obtained in carbonate solutions.

It is well-known that the solubility of UO_2 is very low. Baes and Mesmer¹⁸ give $\log K_{s0} = -1.8$ for the equilibrium



This value is in fair agreement with our own experimental determination, $\log K_{s0} = -2.1$, based on Fuger's¹⁷ value for the $\text{UO}_2^{2+}/\text{U}^{4+}$ couple.

A combination of this value with that of $\log \beta_5$ indicates that the concentrations of U(IV) in equilibrium with UO_2 is very small. Hence, $\text{UO}_2(\text{s})$ is expected to precipitate under the experimental conditions chosen in this study. The absence of precipitate in our solutions is probably due to the fact that the crystalline UO_2 is formed via the precipitation of an amorphous oxide hydrate with a much higher solubility and that the test solutions thus are unsaturated with respect to $\text{UO}_2(\text{s}, \text{amorphous})$.¹⁹ The value of β_5 also suggests that the previously reported formation constant of PuCO_3^{2+} ($\log \beta_1 = 47$) is much too large.

Possible Occurrence of $\text{U}(\text{CO}_3)_5^{6-}$ in Groundwater. A common process for the formation of many uranium ores is weathering of granitic rocks by carbonate-containing, oxygen-rich surface water, followed by a transport of released uranium as $\text{UO}_2(\text{CO}_3)_3^{4-}$ in groundwater. The uranium is then precipitated when the water reaches a reducing zone. A continued redissolution and reprecipitation may occur as a result of changes in the redox state at the precipitation zone.

Transport of thorium in alkaline groundwaters has also been discussed in terms of the formation of soluble carbonate complexes.²⁰ From the equilibrium data obtained in the present study, we can get an estimate of the concentration of carbonate complexes and, hence, their importance for the transport of tetravalent actinoids in groundwater. In groundwater with $\log h = -8$, the total carbonate 2×10^{-3} M (120 ppm), and the redox potential -300 mV (a reasonable value, if the redox potential is determined by Fe(II)/Fe(III) mineral equilibria), the ratio $[\text{U(IV)}]/[\text{U(VI)}]$ is equal to $10^{-8.4}$. Hence, soluble uranium(IV) carbonate species are in general not important for groundwater transport of uranium. The maximum concentration of thorium under the same conditions is of the magnitude 10^{-7} M (~ 20 ppm), a figure that could well account for a large part of the soluble thorium found in groundwater.²¹

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Registry No. $\text{UO}_2(\text{CO}_3)_3^{4-}$, 17872-00-3; $\text{U}(\text{CO}_3)_5^{6-}$, 85662-13-1.

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