

In other words we would need to invoke an activated complex with two entering ligands, one of them acting to labilize the Os(II) center but not disposed to enter the coordination sphere. It seems prudent to defer further speculation until the system and related ones have been more thoroughly explored. The datum at the lowest isonicotinamide concentration can be taken as being the most directly related to the specific rate for reaction 1. The value of specific rate calculated from it is $0.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, to be compared to $1.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for Cl^- as entering group. A factor of 100 is not unreasonable as resulting from the difference in charge between the two entering groups, and in this respect at least, our observations are not out of line.

In the matter of substitution lability, a remarkable qualitative result is the rapidity with which the CO complex is formed. Referring back to the procedure which was followed, when CO is present at atmospheric pressure—corresponding perhaps to 10^{-3} M in methanol solution—reaction is largely complete in 5 min. Even on the assumption that the half-life is 5 min, the second-order specific rate is calculated as ca. 3, to be compared to 0.9×10^{-5} for isn. A large factor directly

involved in the rate difference is that, in the CO case, the reactant species is $\text{BzOsCl}_2\text{CH}_3\text{OH}$, and the labilizing effect of the two chloride ions is being exploited in the facile substitution. The labilizing effect of $\text{NH}_2\text{CH}_2\text{CO}_2^-$ as compared to en has already been noted.

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Registry No. $[\text{BzOs}(\text{NH}_3)_3](\text{PF}_6)_2$, 75700-71-9; $[\text{BzOs}(\text{NH}_3)_2\text{Cl}](\text{PF}_6)$, 75700-73-1; $[\text{BzOs}(\text{en})\text{Cl}](\text{PF}_6)$, 75700-75-3; $[\text{BzOs}(\text{en})\text{Br}](\text{PF}_6)$, 75700-77-5; $[\text{BzOs}(\text{en})\text{NH}_3](\text{PF}_6)_2$, 75700-79-7; $[\text{BzOs}(\text{en})(\text{isn})](\text{PF}_6)_2$, 75700-81-1; $[\text{BzOs}(\text{en})(\text{imid})](\text{PF}_6)_2$, 75700-83-3; $[\text{BzOs}(\text{en})(\text{py})](\text{PF}_6)_2$, 75700-85-5; $\text{BzOs}(\text{gly})\text{Cl}$, 75700-86-6; $\text{BzOs}(\text{CH}_3\text{CN})\text{Cl}_2$, 72765-28-7; $[\text{BzOs}(\text{CH}_3\text{CN})_3](\text{PF}_6)_2$, 75700-88-8; $\text{BzOs}(\text{isn})\text{Cl}_2$, 75700-89-9; $\text{BzOs}(\text{isn})\text{Br}_2$, 75700-90-2; $[\text{BzOs}(\text{isn})_2\text{Cl}]\text{PF}_6$, 75716-24-4; $[\text{BzOs}(\text{isn})_2\text{Br}]\text{PF}_6$, 75700-92-4; $[\text{BzOs}(\text{imid})_2\text{Cl}]\text{PF}_6$, 75700-94-6; $\text{BzOs}(\text{py})\text{Cl}_2$, 75700-95-7; $\text{BzOs}(\text{py})\text{Br}_2$, 75700-96-8; $\text{BzOs}(\text{CO})\text{Cl}_2$, 75700-97-9; $\text{BzOs}(\text{Me}_2\text{SO})\text{Cl}_2$, 75700-98-0; $\text{BzRu}(\text{isn})\text{Cl}_2$, 75700-99-1; $[\text{BzRu}(\text{en})\text{Cl}](\text{PF}_6)$, 75701-00-7; $[\text{BzOs}(\text{en})(\text{H}_2\text{O})](\text{PF}_6)_2$, 75701-02-9; BzOsCl_2 , 53886-43-4; BzOsBr_2 , 75701-03-0; BzOsI_2 , 75701-04-1; $[\text{BzOs}(\text{H}_2\text{O})_3]^{2+}$, 75701-05-2; $[\text{BzRu}(\text{H}_2\text{O})_3]^{2+}$, 75701-06-3; $[\text{BzOs}(\text{NH}_3)_2\text{H}_2\text{O}]^{2+}$, 75701-07-4; $[\text{BzRu}(\text{en})\text{H}_2\text{O}]^{2+}$, 75701-08-5; $[(\text{NH}_3)_5\text{Os}(\text{isn})]^{2+}$, 70252-43-6; $[(\text{NH}_3)_5\text{Os}(\text{py})]^{2+}$, 70252-47-0; $[\text{BzRuCl}_2]_2$, 37366-09-9; ammonium hexachloroosmate(IV), 12125-08-5.

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The First Acidification Step of the Tris(carbonato)dioxouranate(VI) Ion, $\text{UO}_2(\text{CO}_3)_3^{4-}$

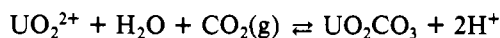
LIBERATO CIAVATTA, DIEGO FERRI, INGMAR GRENTHE,* and FRANCESCO SALVATORE

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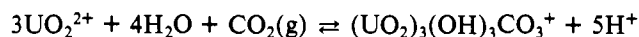
Potentiometric measurements with a glass electrode combined with solubility determinations of $\text{CO}_2(\text{g})$ have indicated that, at 25 °C in 3 M NaClO_4 medium with $[\text{U}(\text{VI})] < 0.05 \text{ M}$ and $\log [\text{HCO}_3^-] \geq -1.2$, the prevailing form of uranium(VI) is the species $\text{UO}_2(\text{CO}_3)_3^{4-}$ ($=\text{UO}_2(\text{OH})_6(\text{CO}_2)_2^{4-}$). On acidification of $\text{UO}_2(\text{CO}_3)_3^{4-}$, and before solid uranyl carbonates start to precipitate, a polynuclear complex $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ ($=(\text{UO}_2)_3(\text{OH})_{12}(\text{CO}_2)_6^{6-}$) was found to form according to $3\text{UO}_2(\text{CO}_3)_3^{4-} + 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{CO}_3)_6^{6-} + 6\text{HCO}_3^-$ with the equilibrium constant, $\log \beta_{3,12,6} = -6.43 \pm 0.08$. No evidence for the species $\text{UO}_2(\text{CO}_3)_2^{2-}$ or mixed species $(\text{UO}_2)_p(\text{OH})_q(\text{CO}_3)_r$ was obtained in the experimental range investigated: $10^{-3} \leq [\text{U}(\text{VI})] \leq 0.03 \text{ M}$, $0.1 \leq P_{\text{CO}_2} \leq 1 \text{ atm}$, and $-3.0 \leq \log [\text{HCO}_3^-] \leq -0.7$. The ^{13}C NMR spectra of the two complexes indicate the presence of three equivalent carbonate groups in the mononuclear complex and two different carbonate sites with the ratio 1:2 between the integrated intensities in the trinuclear complex. The NMR data are compatible with a structure containing both bridging and terminal carbonate groups.

Introduction

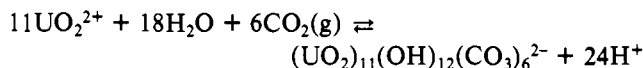
The equilibria between UO_2^{2+} , H_2O , and $\text{CO}_2(\text{g})$ at 25 °C have been previously¹ studied in a 3 M NaClO_4 medium at acidities ranging from $[\text{H}^+] = 10^{-3} \text{ M}$, where complexing is negligible, to $[\text{H}^+] = 10^{-4.8} \text{ M}$, when a precipitate of U(VI) carbonates starts to form. The extensive data collected were interpreted by assuming the formation of the carbonate complexes: UO_2CO_3 , $(\text{UO}_2)_3(\text{OH})_3\text{CO}_3^+$, and a large species, probably $(\text{UO}_2)_{11}(\text{OH})_{12}(\text{CO}_3)_6^{2-}$. The following equilibrium constants were determined:



$$\log \beta_{1,2,1} = -9.02$$



$$\log \beta_{3,5,1} = -16.34$$



$$\log \beta_{11,24,6} = -72.0$$

Exploratory experiments indicated that the precipitate of uranium(VI) carbonates redissolves at lower acidities and that clear solutions result at $[\text{H}^+] < -5.7 \text{ M}$, provided the equilibrium pressure of $\text{CO}_2(\text{g})$ is $>10^{-2} \text{ atm}$. These figures are somewhat dependent on $[\text{U}(\text{VI})]$ but are not likely to change dramatically in the U(VI) concentrations between 10^{-3} and 0.1 M.

Previous workers, whose results are reviewed in ref 1, generally agree in assuming $\text{UO}_2(\text{CO}_3)_3^{4-}$ as the final result of the reaction.

The aim of the work is the study of the equilibria occurring in the acidity range from the dominance of $\text{UO}_2(\text{CO}_3)_3^{4-}$ to

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(1) Ciavatta, L.; Ferri, D.; Grimaldi, M.; Palombi, R.; Salvatore, F. J. Inorg. Nucl. Chem. 1979, 41, 1175.

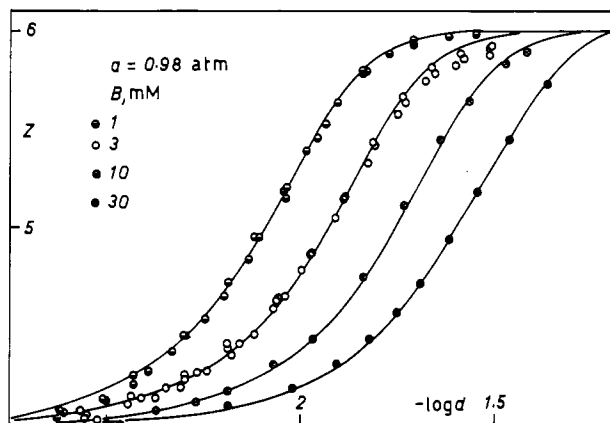


Figure 1. Data at 0.98 atm: Z , the average number of OH^- groups bound per UO_2^{2+} in the $(\text{UO}_2)_p(\text{OH})_q(\text{CO}_2)_r$ species, as a function of $\log d$. Curves calculated with the assumption that $\log \beta_{3,12,6} = -6.37$.

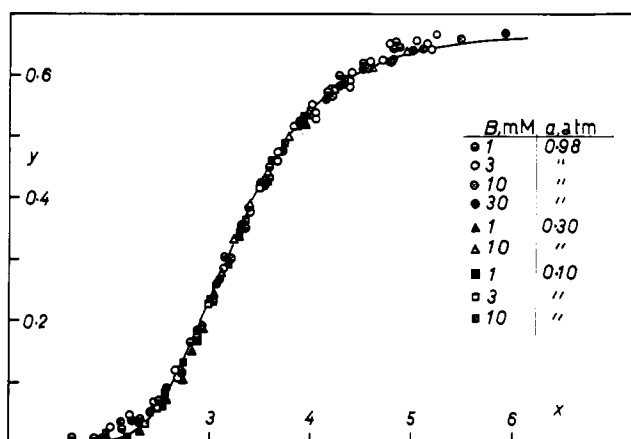
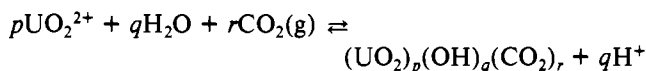


Figure 2. $y (= (6 - Z)/3)$ as a function of $x (= \log B d^3 a^{1.5})$. Curve calculated with the equilibrium constant $\log \beta_{3,12,6} = -6.40$.

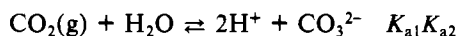
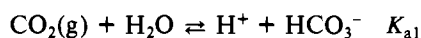
the incipient formation of solid carbonates.

Notations

From an experimental point of view, the uranium(VI) carbonate system is a three-component, rather than a two-component system. The experimentally determined equilibrium quantities are the partial pressure of CO_2 and the hydrogen ion concentration. The most general formula of a complex may then be written as $(\text{UO}_2)_p(\text{OH})_q(\text{CO}_2)_r$, omitting charges for brevity. The equilibrium constant β_{pqr} refers to the reaction



The partial pressure of CO_2 and the hydrogen ion concentration are related through the protolysis constants of $\text{CO}_2(\text{g})$



By using the emf method only, one cannot from a mathematical point of view distinguish between $(\text{UO}_2)_p(\text{OH})_q(\text{CO}_2)_r$ and $(\text{UO}_2)_p(\text{OH})_{q-2}(\text{CO}_3)_r$. When performing the mathematical analysis of the equilibrium data, we will describe the complexes by using the more general $(\text{UO}_2)_p(\text{OH})_q(\text{CO}_2)_r$ terminology.

Table I. Survey of the Solubility Measurements ($a = 0.9705 \pm 0.0005$ Atm)

B , M	H , M	A , M	Z
0.0	6.2×10^{-3}	0.0193 ± 0.0002	
0.01018	-0.1306	0.120 ± 0.001	6.00
0.01016	-0.1313	0.120 ± 0.001	6.00
0.0300	-0.1417	0.093 ± 0.001	4.30

Table II. $F_{3,12}$ Values Calculated by Curve Fitting with Eq 7 and 8

a , atm	0.977	0.295	0.0997
$-\log F_{3,12}$	6.33 ± 0.06	4.80 ± 0.06	3.35 ± 0.06

a = partial pressure of $\text{CO}_2(\text{g})$ at equilibrium

A = total carbonate concentration

b = concentration of UO_2^{2+}

B = total concentration of U(VI)

c = concentration of $\text{UO}_2(\text{CO}_3)^{4-} (= \text{UO}_2(\text{OH})_6(\text{CO}_2)_3^{4-})$

c_0 = concentration of $\text{UO}_2(\text{OH})_6 = \sum [\text{UO}_2(\text{OH})_6(\text{CO}_2)_r]$

d = concentration of HCO_3^-

h = concentration of H^+

H = analytical excess of H^+ over H_2O , CO_2 , and UO_2^{2+}

Z = average number of H^+ split off per $\text{UO}_2^{2+} = (h - H - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}])B^{-1}$

$K_{pq} = \sum r \beta_{pqr} a^r$

β_{pqr} = equilibrium constant for $p\text{UO}_2(\text{OH})_6(\text{CO}_2)_3 + (r + 3p - q)\text{CO}_2(\text{g}) \rightleftharpoons (\text{UO}_2)_p(\text{OH})_q(\text{CO}_2)_r + (6p - q)\text{HCO}_3^-$

F_{pq} = equilibrium constant for the formation of the $(\text{UO}_2)_p(\text{OH})_q$ group of complexes: $p\text{UO}_2(\text{OH})_6 + (6p - q)\text{CO}_2(\text{g}) \rightleftharpoons (\text{UO}_2)_p(\text{OH})_q + (6p - q)\text{HCO}_3^-$

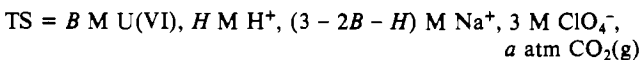
Concentration and equilibrium are expressed on the molar scale.

Method

For a study of the equilibria, the hydrogen carbonate concentration d was measured at 25 °C with the use of a glass electrode in solutions of various B and H and saturated with $\text{CO}_2(\text{g})$ of various partial pressures. From the emf data the function $Z(\log d)_{B,a}$, which forms the basis of the following treatment, was obtained. In a few solutions of accurately known Z and d , the solubility of $\text{CO}_2(\text{g})$ was determined. These experiments served to check the number of carbonate ions in the formula of the reaction products.

The potentiometric measurements were carried out as titrations. During a titration B and a were kept constant while H was varied by adding HClO_4 or, in back-titrations, NaHCO_3 . (A stream of $\text{CO}_2(\text{g})$ or of $\text{CO}_2\text{-N}_2$ mixture was passed through the test solution. During the performance of each of the titrations, the atmospheric pressure, hence a , changed by no more than 0.2–0.3%. This constancy is sufficient for our purposes.)

In our solutions a constant ionic medium was maintained in order to minimize variations of the activity coefficients and, consequently, to be able to use concentrations instead of activities in the equilibrium conditions. A 3 M $(\text{Na})\text{ClO}_4$ medium was used in order to conform with the conditions chosen in the previously studied UO_2^{2+} carbonate equilibria in acid solution.¹ The test solutions had therefore the general composition



In this work B ranged from 3×10^{-2} to 10^{-3} M. Higher values were not included in order to avoid large changes in the medium. At $B < 10^{-3}$ M, data of sufficient accuracy could not be obtained because the difference between d and H which determines the accuracy of Z is close to zero. The partial pressure of $\text{CO}_2(\text{g})$ covers the interval from 1 to 0.1 atm. The lower limit was imposed by the slow attainment of equilibrium, while the fragility of the glass apparatus renders impracticable the measurements at $a > 1$ atm. Finally, d was varied from low enough values where no solid uranium(VI) carbonates are present to sufficiently high concentrations, e.g., 0.05 M, for which still accurate Z values can be calculated within the accuracy of the emf measurements, ± 0.02 mV. (In a forthcoming paper, a spectrophotometric study on the uranyl-carbonate system is described

in which evidence will be given that no other species are formed, up to $\log h = -12$, than those found in this investigation.) The equilibrium concentration of HCO_3^- , d , was determined by means of the cell



where GE stands for glass electrode and

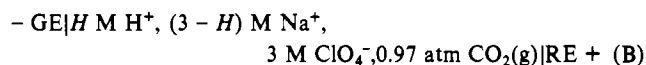


Taking into account the equilibrium $\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ allows the emf of cell A in mV to be written at 25 °C as in eq 1 where

$$E = E^\circ - 59.16 \log a + 59.16 \log d + 59.16 \log f_{\text{HCO}_3^-} + E_j \quad (1)$$

E° is a constant, $f_{\text{HCO}_3^-}$ is the activity coefficient of HCO_3^- , and E_j is the liquid junction potential between TS and 3 M NaClO_4 . The standard states are so chosen that $f_{\text{HCO}_3^-}$ as well as the activity coefficients of other reacting species approach 1 as the composition of TS approaches 3 M NaClO_4 .

It is to be expected, according to the specific interaction theory,² that $f_{\text{HCO}_3^-}$ is practically unity in dilute B and H solutions, provided the sodium level is kept constant. Furthermore, since bicarbonate and other species in TS are present in low concentrations in comparison with those of Na^+ and ClO_4^- , the E_j term in eq 1 should be negligible when $[\text{Na}^+] = \text{constant}$. Under the chosen experimental conditions the $[\text{Na}^+]$ does vary somewhat; thus, changes of both $f_{\text{HCO}_3^-}$ and E_j have to be expected. The dependence of $E_j + 59.16 \log f_{\text{HCO}_3^-}$ on $\Delta[\text{Na}^+]$ (in general $\Delta[\text{Na}^+] = -H - 2B$) was determined by measuring the emf of cell B as a function of H in the range between -10^{-3} and



-0.3 M . The concentration of HCO_3^- in these test solutions was calculated by means of eq 2 by using $\log K_{a1} = -7.987 \pm 0.001$,

$$h - H = d + 2(K_{a2}d^2/K_{a1}a) \quad (2)$$

evaluated by us, and $\log K_{a2} = -9.63$, as determined by Frydman et al.³ under identical experimental conditions, and neglecting h . Thus, the plot of $E - 59.16 \log d$ vs. $\Delta[\text{Na}^+]$ was constructed. The data could be fitted with a straight line of slope -7.2 ± 0.2 within the limits of experimental error.

We may thus conclude that in our solutions the emf of cell A is approximated by eq 3. Each titration consists of three parts. In the

$$E = E^\circ - 59.16 \log a + 59.16 \log d - 7.2\Delta[\text{Na}^+] \quad (3)$$

first part, the emf measurements are performed in solutions with $B = 0$, where the concentration of HCO_3^- is varied within at least a factor of 10. These data served to assess E° with use of (2) and (3). In every case E° values within $\pm 0.03 \text{ mV}$ were found. Then U(VI) was introduced and the titration continued by adding HClO_4 or NaHCO_3 in back-titrations. Since E° is known, d and then Z were calculated for every point. Finally, for a check of the H value, an excess of standardized HClO_4 was added and the potentiometric measurements were performed in solutions of $h > 10^{-3} \text{ M}$. The analytical excess of H^+ was calculated on the basis of Gran⁴ plots.

Experimental Section

Materials and Analysis. The starting material for the preparation of uranium(VI) perchlorate solutions was U_3O_8 , obtained by ignition at 900 °C of $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ (Merck p.a.). The oxide, suspended in a slight excess of HClO_4 , was dissolved at an appreciable rate by iodic acid [$5\text{U}_3\text{O}_8(\text{s}) + 2\text{HIO}_3 + 30\text{H}^+ \rightarrow 15\text{UO}_2^{2+} + \text{I}_2(\text{s}) + 16\text{H}_2\text{O}$], and the iodine was entirely removed by heating. The preparations were performed with a small deficit of HIO_3 to avoid the presence of IO_3^- at the end of the reaction, and the undissolved U_3O_8 was finally eliminated by filtration. The clear solution proved to be free of IO_3^- , I^- , Cl^- , and Fe(III) .

The uranium(VI) concentration in the stock solution was determined gravimetrically as U_3O_8 by precipitation with gaseous ammonia and by igniting the precipitate at 900 °C. For an analysis of the proton excess, H , a weighed quantity of stock solution was added to 3 M NaClO_4 containing OH^- generated coulometrically, in a sufficient amount to neutralize H , approximately. The resulting solution was then titrated potentiometrically with a glass electrode by H^+ produced coulometrically. The end point was established via Gran⁴ diagrams. The total ClO_4^- was evaluated as $2B + H$.

Perchloric acid solutions were made by diluting a 70% Merck p.a. product and were standardized against Ti_2CO_3 . The results of the analyses coincided with 0.05%.

Sodium hydrogen carbonate solutions made from the Merck p.a. preparation were analyzed with standard HClO_4 .

Sodium perchlorate was prepared by following the procedure suggested by Biedermann⁵ with the modification that the stock solution was made to contain a slight amount of H^+ , about 10^{-3} M . Thereby, the dissolution of glass components from the containers could be kept at a minimum. The H^+ concentration was analyzed via Gran⁴ plots from potentiometric titrations with OH^- produced coulometrically. The salt concentration of the stock solution was determined by weighing samples dried at 125 °C.

Silver perchlorate solutions from Ag_2CO_3 and HClO_4 were standardized potentiometrically against NaCl .

Sodium hydroxide solutions, made by diluting a clear 50% NaOH solution in a nitrogen atmosphere, were analyzed with standard HClO_4 . For equilibration of the test solution with carbon dioxide of the required partial pressure, commercially available $\text{CO}_2\text{-N}_2$ mixtures of known compositions were employed. The gas was purified by passing it through 10% H_2SO_4 , H_2O , 3 M NaClO_4 , and a G4 glass filter. The gas composition was periodically checked by treating dried samples with standard Ba(OH)_2 in excess and titrating the excess of the base with HClO_4 to the phenolphthalein end point. It may be concluded on the basis of these analyses that the CO_2 concentration coincides within 1% with the specified value. The values of a were evaluated by multiplying the CO_2 percentage by the following difference: atmospheric pressure - vapor pressure of water in 3 M NaClO_4 (0.0276 atm at 25 °C).

Measurements. All the emf measurements were performed in a silicone oil thermostat kept at 25.00 ± 0.01 °C. The cell arrangement was similar to that described by Forsling et al.⁶ The Ag,AgCl electrodes were prepared according to Brown.⁷ The glass electrodes, Beckman, were of the type GP. The E values were measured with a precision of 0.01 mV by using a Dynamco Ltd. 2022 Digital voltmeter.

After the addition of the reagent, E became constant within 30–40 min and remained constant within 0.05 mV for at least 12 h. The time required to attain a steady E value depends on the partial pressure of $\text{CO}_2(\text{g})$. At $a < 0.1 \text{ atm}$, the time to attain the equilibrium potentials became too long to make the titration procedure practical. The reproducibility of E was in any case better than 0.1 mV.

The reversibility of the reactions was tested by back-titrations. The coincidence of the data, within the limit of experimental error, with those of the forward titrations indicated that true equilibrium was attained.

The ^{13}C NMR spectra were obtained at 25 °C with use of a Bruker WP200 with a superconducting magnet. The total concentration of uranium in the samples was 0.010 M. About 20 000 transients were accumulated, the repetition rate was 0.5 pulse/s.

Solubility Determination of $\text{CO}_2(\text{g})$. The gas, purified and pre-saturated as described above, was bubbled through the test solution placed in a long tube which was maintained at 25.00 ± 0.05 °C. After saturation, which was accomplished within 24 h, samples were withdrawn by a pipet. In order to avoid underpressure during sampling, the pipet was completely immersed in the solution, until its mark went 1–2 cm under the liquid level. The total carbonate concentration was determined by following essentially the procedure suggested by Pieters.⁸ By this approach, which was tested with KHCO_3 as standard substance, samples of 1 mmol of CO_2 could be analyzed with an accuracy of $\pm 1\%$. For each test solution at least three samples were analyzed.

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(3) Frydman, M.; Nilsson, G.; Rengemo, T.; Sillén, L. G. *Acta Chem. Scand.* **1958**, *12*, 878.
(4) Gran, G. *Analyst (London)* **1952**, *77*, 661.

(5) Biedermann, G. *Ark. Kemi* **1956**, *9*, 277.

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(8) Pieters, H. A. J. *Anal. Chim. Acta* **1948**, *2*, 263.

Treatment of the Data and Results

The supplementary material gives the whole set of the $Z(\log d)_{B,a}$ data. In Table I, the solubility measurements are summarized.

The experimental data were treated as follows. First (section I), the predominant sets (p,q) were deduced by treating the emf data pertaining to experiments with $\text{CO}_2\text{-N}_2$ mixtures of the same composition, separately. Then (section II), the predominant r values were calculated by analyzing the $Z(\log d, a)_B$ functions and, more directly, from the solubility determinations of Table I. Finally (section III), the whole set of the potentiometric data was treated simultaneously by comparing them with normalized model functions and by using the generalized least-squares program LETAGROP.⁹

I. Evaluation of the Predominant p and q Values. In all our titrations with $\text{CO}_2\text{-N}_2$ mixtures of the same composition, the atmospheric pressure changes do not introduce a variation in a exceeding 2%. We may thus simplify the calculations without introducing any appreciable error by using rounded-off a values. Hence, the main a levels are 0.977 ± 0.014 , 0.295 ± 0.001 , and 0.0997 ± 0.0004 atm.

If a is constant, our four-variable system $Z(B,a,d)$ is transformed into a three-variable one $Z(B,d)$, and the predominant (p,q) values may conveniently be obtained by the graphical methods developed by Sillén.¹⁰

As seen in Figure 1, the curves of $Z(\log d)_B$ at $a = 0.977$ atm are parallel within the limit of experimental error in the whole Z range investigated. Similar conclusions could be drawn from the data at $a = 0.295$ and $a = 0.0997$ atm. From the spacing between the curves

$$((\Delta \log B)/(\Delta \log d))_Z = -((\Delta \log B)/(\Delta \log h))_Z = 3.0$$

we deduce the general formula of the complexes: $(\text{OH})_s\text{-}[\text{UO}_2(\text{OH})_t]_n$, where t is a constant and s is a variable. The most probable values of t and s may be calculated from the limiting Z .

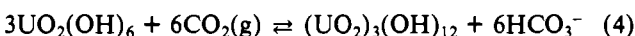
The Z curves range between 4 and 6. The complexes at these limits may be species of the type $[\text{UO}_2(\text{OH})_6]_n$ and $[\text{UO}_2(\text{OH})_4]_m$, and for the continued treatment of the data, it is convenient to start with one of these limiting species. Since a concentrated U(VI) solution becomes more acid (d decreases) on dilution (Figure 1), we concluded that the complexes at $Z \rightarrow 6$ are of lower nuclearity than those at $Z \rightarrow 4$ ($n < s < m$). We then have

$$Z(\rightarrow 6) = (3 + tn)/n$$

$$Z(\rightarrow 4) = (3 + tm)/m$$

if $n = 1$, $t = 3$, and $m = 3$. The condition $n > 1$ gives, on the other hand, negative m values. Thus, the complexes dominating at $Z = 6$ are $(1,6,r)$, while at $Z = 4$, $(3,12,r')$ prevail.

Next, we attempted to explain our data in the simplest way by assuming the existence of the limiting complexes only, $\text{UO}_2(\text{OH})_6$ and $(\text{UO}_2)_3(\text{OH})_{12}$. This hypothesis was tested by comparing the $Z(\log d)_B$ data with model functions calculated by the following procedure. Since, in the concentration range studied, the free concentration of UO_2^{2+} is negligible, according to Sillén¹⁰ it is more convenient to write the equilibrium condition with the complex of lower nuclearity as reagent



$$[(\text{UO}_2)_3(\text{OH})_{12}] = F_{3,12}c_0^3d^{-6}a^6$$

where

$$F_{3,12} = K_{3,12}K_{a1}^6K_{1,6}^{-3}$$

$F_{3,12}$ is the conditional constant for the formation of the species having 3U and 12OH⁻ groups but a variable number of CO₂. We then have for the Z expression

$$Z = (6 + 12F_{3,12}c_0^2d^{-6}a^6)/(1 + 3F_{3,12}c_0^2d^{-6}a^6) \quad (5)$$

Introducing the new variable

$$u^2 = F_{3,12}c_0^2d^{-6}a^6 \quad (6)$$

the theoretical $Z(X)$ curves

$$Z = (6 + 12u^2)/(1 + 3u^2) \quad (7)$$

$$X = \frac{1}{3} \log u + \frac{1}{3} \log (1 + 3u^2) - \frac{1}{3} \log B \\ = \frac{1}{6} \log F_{3,12} - \log (d/a) \quad (8)$$

were calculated for each B . When the family of $Z(X)_B$ curves was imposed on the maps $Z(\log (d/a))_B$ and moved along the X axis, a satisfactory fit was found in the entire Z and a ranges. We may thus conclude that the data of present accuracy may be explained with the formation of $(1,6,r)$ and $(3,12,r')$.

The most probable $F_{3,12}$ values, evaluated from the difference $X - \log a + \log d$, read off in the position of best fit, are collected in Table II.

II. Evaluation of the Most Important r and r' Values. The number of CO₂ groups present in the $(1,6,r)$ and $(3,12,r')$ complexes was evaluated (a) by analyzing the $Z(\log h, a)$ functions at constant B and (b) from the solubility data of Table I.

The $Z(\log h, a)$ ($h = K_{a1}a/d$) plots, at constant B , were parallel with the spacing, $((\Delta \log a)/(\Delta \log h))_{Z,B} = 2.0$. This means¹⁰ that all the predominating complexes have in their formula two OH⁻ groups per CO₂. We may thus infer that the complexes are $\text{UO}_2(\text{OH})_6(\text{CO}_2)_3$ and $(\text{UO}_2)_3(\text{OH})_{12}(\text{CO}_2)_6$.

These results are corroborated by the direct determination from solubility measurements of Table I. Assuming that a single r , R , and single r' , R' , represent the series of values in the species $(1,6,r)$ and $(3,12,r')$, respectively, allows the stoichiometric condition for solutions saturated with CO₂ to be written as

$$BZ = h - H - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] = \\ 6[\text{UO}_2(\text{OH})_6] + 12[(\text{UO}_2)_3(\text{OH})_{12}]$$

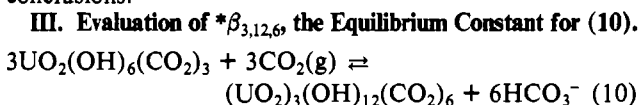
$$A = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + R[\text{UO}_2(\text{OH})_6] + \\ R'[(\text{UO}_2)_3(\text{OH})_{12}]$$

$$B = [\text{UO}_2(\text{OH})_6] + 3[(\text{UO}_2)_3(\text{OH})_{12}]$$

By rearranging and neglecting h and $[\text{CO}_3^{2-}]$ (this quantity accounts only for 0.1% of A), we have

$$BZ + H + A - [\text{H}_2\text{CO}_3] = \\ RB(Z - 4)/2 + R'B(6 - Z)/6 \quad (9)$$

from which R and R' were estimated. First, from the determinations at $Z = 6.0$, taking for $[\text{H}_2\text{CO}_3]$ the CO₂(g) solubility in 3 M NaClO₄, we found $R = 3.0 \pm 0.1$. Then the measurements at $Z = 4.30$, introducing $R = 3$ in (9), gave $R' = 5.7 \pm 0.4$, in substantial agreement with the above conclusions.



The calculations presented in the foregoing sections have furnished evidence for the main uranium(VI) species in NaHCO₃ solutions being $\text{UO}_2(\text{OH})_6(\text{CO}_2)_3$ and $(\text{UO}_2)_3(\text{OH})_{12}(\text{CO}_2)_6$. Due to the negligible concentration of UO_2^{2+} ,

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which we have not been able to determine experimentally, the formation constants $\beta_{1,6,3}$ and $\beta_{3,12,6}$ cannot be deduced from our experimental data. However, the present measurements may conveniently be described by $*\beta_{3,12,6}$, the constant of equilibrium 10 written with the species of lower nuclearity as reagent.

Values of $*\beta_{3,12,6}$ can be obtained from $\log F_{3,12} + 3 \log a = \log K_{al} \beta_{3,12,6} \beta_{1,6,3}^{-3} = \log * \beta_{3,12,6}$. Using the data of Table II, we find $\log * \beta_{3,12,6} = -6.37 \pm 0.08$.

It was desirable to compare the whole set of emf data directly with model curves as such a comparison enables us to evaluate the magnitude of the uncertainty of the equilibrium constant. As a check of the consistency of the graphical results, the data were finally treated with the generalized least-squares program LETAGROP.⁹ The graphical approach consisted of comparing the data recalculated in the form $y(x)$, $y = (6 - Z)/3$ and $x = \log (Bd^{-3}a^{1.5})$, with the normalized $Y(X)$ function

$$Y = 2v^2/(1 + 3v^2) \quad (11)$$

$$X = x + \frac{1}{2} \log * \beta_{3,12,6} = \log v + \log (1 + 3v) \quad (12)$$

Equations 11 and 12 were easily derived by introducing in the expression of $y(x)$ the new variable

$$v^2 = * \beta_{3,12,6} c^2 d^{-6} a^3 \quad (13)$$

In position of best fit, shown in Figure 2, we calculated from the difference $X - x$

$$\log * \beta_{3,12,6} = -6.40 \pm 0.08$$

For the numerical treatment, we used the most recent version, ETITR, of LETAGROP.⁹ The calculations consisted of the minimization of the sum $\sum (H - H_{\text{calcd}})^2$, where H_{calcd} is the value of H calculated with a particular $*\beta_{3,12,6}$. The minimum sum was found with $\log * \beta_{3,12,6} = -6.43 \pm 0.03$, which is seen to agree well with the graphical evaluation. The uncertainty of the LETAGROP constant is 3 times the standard deviation. Of 146 experimental points considered, 76 have shown negative and 70 positive deviations from the calculated H . The average positive deviation $\delta H/H$ amounts to 0.21%; the negative to 0.26%. The sign and the magnitude of the deviations do not exhibit any systematic trend with B and d . Since the average deviation of H is just above its experimental accuracy, $\pm 0.1\%$, we may conclude that the data can be quite satisfactorily explained with equilibrium 10.

Structure and Bonding of the Uranyl Carbonate Complexes

The stoichiometry of the uranyl carbonate complexes formed in the solutions studied are $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$. Through a ¹³C NMR investigation of solutions containing these complexes as dominating species, we were able to get some idea of the bonding of the carbonate ligand.

The mononuclear complex has one single ¹³C resonance peak indicating equivalence between the three coordinated ligands. In the solid state, the $\text{UO}_2(\text{CO}_3)_3^{4-}$ group consists of three bidentate ligands coordinated in a plane perpendicular to the UO_2 axis.¹¹ The NMR data are consistent with this model. Quantitative information about the solution structure may be obtained by an X-ray diffraction study of concentrated $\text{UO}_2(\text{CO}_3)_3^{4-}$ solutions, the results of such a study will be published in the near future.

The trinuclear complex gives two separate ¹³C NMR peaks with the ratio 1:2 between the integrated intensities. The smaller peak has approximately the same chemical shift as the carbonate groups in the mononuclear complex, while the other is displaced 70 Hz toward higher frequency. The NMR data indicate the presence of both bridging and terminal carbonate groups. The terminal carbonate groups are probably chelating.

More detailed structure information will be presented in a forthcoming X-ray structure investigation of the complex in solution. In this study, we also hope to obtain evidence for the location of coordinated water molecules.

There is no evidence for exchange broadening, neither between the two sites in the trinuclear complex nor between the mono- and trinuclear complexes. A more detailed NMR study will be presented in a following publication.

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Registry No. $\text{UO}_2(\text{CO}_3)_3^{4-}$, 17872-00-3; $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, 75311-41-0.

Supplementary Material Available: A listing of primary experimental data in the form of $Z(\log d)$ at various B and a levels (3 pages). Ordering information is given on any current masthead page.

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Mechanism of Dissociation of Alkynes from Some Platinum-Alkyne Complexes

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Five-coordinate platinum-alkyne complexes $[\text{PtXMe}(\text{RC}\equiv\text{CR})(2,2'\text{-bpy})]$ (bpy = 2,2'-bipyridine) have been prepared and characterized. An investigation of the kinetics and mechanism of thermal dissociation of alkyne from these complexes has been made. When $\text{X} = \text{Cl}$ and $\text{R} = \text{CO}_2\text{Me}$, the rate of reaction is very strongly accelerated in more polar solvents and is retarded by added chloride, and a mechanism involving preliminary ionization of chloride is proposed. However, when $\text{X} = \text{Cl}$ or I and $\text{R} = \text{CF}_3$, the rate is essentially independent of solvent polarity and is not retarded by added halide, and a nonpolar intermediate is proposed in this case.

Introduction

During investigations of the reactions of alkyl(2,2'-bipyridine)platinum(II) complexes with alkenes and alkynes,²⁻⁵

it was found that solutions of $[\text{PtClMe}(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})(\text{bpy})]$ underwent dissociation of alkyne much more

(1) (a) University of Liverpool. (b) University of Western Ontario.

(2) N. Chaudhury and R. J. Puddephatt, *J. Organomet. Chem.*, **84**, 105 (1975).