

The scope of this behavior and the factors that determine the relative contributions of quartet vs. doublet photochemistry remain to be delineated.

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Hydrolysis and Carbonate Complexation of Dioxouranium(VI) in the Neutral-pH Range at 25 °C¹

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A review of the data on the hydrolysis and carbonate complexation of uranyl(VI) ion, which are critical to any model attempting to describe the migration behavior of uranium in the geosphere, shows general agreement in regard to the existence of the following species:^{2a} UO₂²⁺, UO₂(OH)⁺, (UO₂)₂(OH)₂²⁺, (UO₂)₃(OH)₅⁺, UO₂CO₃, UO₂(CO₃)₂²⁻, and UO₂(CO₃)₃⁴⁻. Stability constants of the hydrolysis products^{2b} were obtained by potentiometric titrations up to a pH of 4.5, which marks the onset of precipitation of uranates. On the other hand, carbonate complexation constants have been derived from systems containing relatively high concentrations of this ligand. The uranium-carbonate system is also subject to the formation of solids near the neutral-pH region. It is apparent that an accurate representation, in an attempt to describe the behavior of uranium in natural waters on the basis of those species listed above, could not be made without some certainty that other species are not present in the neutral range and at relatively low partial pressures of CO₂ that are more representative of the medium under consideration. Tsymbal,³ in a study of carbonate complexation of the uranyl ion, performed potentiometric titrations that covered the neutral range and detected species additional to those listed above. He explained the data with the inclusion of (UO₂)₃(OH)₇⁻ and UO₂(CO₃)OH⁻. Reports on the existence of another species in the neutral range were also made by Blake et al.⁴ on the basis of spectrophotometric observations. These workers proposed U₂O₅(CO₃)OH⁻ as the formula for this species. The observations regarding this species were of a qualitative nature, and no attempt was made to obtain its stability constant. Finally, Porter⁵ also proposed the existence of U₂O₅(CO₃)OH⁻ on the basis of inflection points in plots of pH vs. volume of HCO₃⁻ added to UO₂(NO₃)₂ solutions.

The present study was undertaken in an attempt to clarify the nature of the uranyl species formed in the neutral-pH range at relatively low CO₂ partial pressures; i.e., 10^{-3.5}-10^{-2.0} atm.

Experimental Section

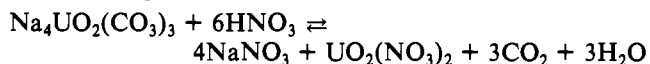
Uranyl dinitrate hexahydrate, Puratronic grade (a highly purified reagent) from Alfa Inorganics was used as starting material to prepare Na₄UO₂(CO₃)₃ according to a procedure described by Tsymbal.³ All other chemicals were AR grade and were used without further purification.

Visible spectra were recorded on a Unicam SP 8-100 spectrophotometer. Cyclic voltammograms were run with a Model 173 potentiostat driven by a Model 175 signal generator both from Princeton Applied Research. pH determinations were done with a Orion Model 701A pH meter using a combination glass electrode. In the potentiometric titrations section of this study the hydrogen ion concentration was determined with an electrode in which the AgCl-saturated 3 M KCl electrolyte filling the electrode was replaced by AgCl-saturated 0.1 M NaClO₄. This was done in order to minimize junction potentials with the titration medium, which contained NaClO₄ as background electrolyte to provide a 0.1 M ionic strength. During the course of the titrations the electrode was calibrated after each titrant addition with a 10⁻³ M HClO₄ solution in 0.1 M NaClO₄. Drift in the calibration readings, which typically were made every 2 h, did not exceed 1 mV. The titrations were conducted in a set of two jacketed cells connected in series and maintained at 25.0 ± 0.1 °C. The cells were provided with a sparge tube through which analyzed gas mixtures containing 0.03, 0.3, and 0.99% CO₂ by volume in nitrogen were passed in separate runs. The first cell served to saturate the gas stream with water vapor while the second was used as the titration vessel. Corrections due to the contribution of the partial pressure of water vapor and the daily changes in atmospheric pressure were taken into account for calculating the equilibrium CO₂ partial pressure for each run. The titrant, 0.1 M HClO₄, was introduced through a Teflon small-bore tube by means of a precision syringe from Micro Metric Instruments Co. A stock solution of 0.01 M U as uranyl tricarbonate with the sodium concentration increased to 0.048 M by the addition of NaHCO₃, for the prevention of hydrolysis, was used in the preparation of the solutions for the titration runs. The ionic strength of these solutions was adjusted to 0.1 M by the addition of NaClO₄.

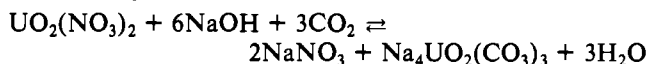
Results and Discussion

Exploratory Experiments. A number of experiments was conducted in order to confirm the presence of uranyl carbonate complexes in the neutral-pH range.

The method employed by Blake et al.⁴ in obtaining the species in question after the addition of 3.5 equiv of HClO₄ to a UO₂(CO₃)₃⁴⁻ solution can be described as an intermediate stage of the process



True equilibrium conditions dictate that the same intermediate stage could be achieved if the above process was reversed as described by



This approach was tried; addition of 2.5 equiv of NaOH/equiv of U to a 0.01 M U solution of uranyl nitrate maintained under 1 atm of CO₂ produced a solution with a pH of 5.0. When excess CO₂ was sparged off with an inert gas, the pH increased to 8.1 and a solution having a visible spectrum identical with that described by Blake et al.⁴ was produced.

Physicochemical changes occurring in the solution as the pH increases during the displacement of excess CO₂ were followed in a number of separate experiments done under the same conditions.

The carbon content of the solution showed an initial sharp drop; but, the change in carbon content as a function of pH slowed down and became asymptotic at a carbon content corresponding approximately to U/CO₃ = 2.0 (cf. Figure 1). The time dependence of the change in pH of the solution, while being sparged with an inert gas at a constant rate, was followed in a separate experiment (Figure 2). The pH values were expressed in terms of carbon content on the basis of the relation

- (1) Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with Union Carbide Corp.
- (2) (a) D. Langmuir, *Geochim. Cosmochim. Acta*, **42**, 547 (1978). (b) C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962).
- (3) C. Tsymbal, *Rapp. CEA-R-Fr., Commis. Energ. At., CEA-R-3476* (1969).
- (4) C. A. Blake, R. S. Lowrie, K. B. Brown, and D. G. Hill, Report ORNL-Y-794, Oak Ridge National Laboratory, Oak Ridge, TN, 1951.
- (5) J. A. Porter, Thesis, Vanderbilt University, 1957.

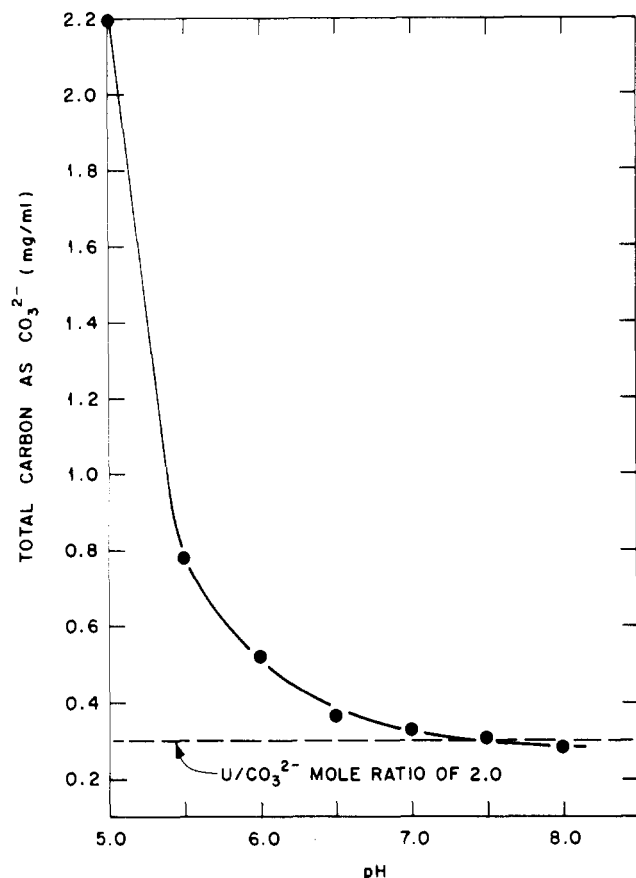


Figure 1. Carbon content of a 0.01 M U solution as a function of pH during the displacement of CO_2 with an inert gas.

between pH and carbon content established in the previous experiments. This transformation highlights the fact that the molar relation of U/CO_3 becomes asymptotic at a value of 2.0.

Spectral changes were followed in a parallel experiment. The initial solution showed a broad band with a maximum at 430 nm having a molar extinction coefficient (based on U) of 63. These values changed to 440 and 100, respectively, as the pH increased to a limiting value of 8.2. Additional sparging did not produce any changes in the spectrum of pH of the solution.

Raman spectra of the solutions were recorded as the CO_2 was displaced with argon. The spectral region of $850 \pm 50 \text{ cm}^{-1}$, corresponding to the range of frequencies of the symmetric stretch of the uranyl ion, was monitored. The initial solution showed a broad band centered at about 845 cm^{-1} . This band became sharper as the pH increased and showed a maximum of 834 cm^{-1} . The interpretation of the Raman spectra is reported elsewhere.⁶ Briefly, the initial spectrum corresponds to the hydrolytic species $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$. The assignment was made on the basis of the work of Toth et al.⁷ As the pH increased and the final stage was reached, the resulting spectrum was assigned to the species $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$. This assignment was made on the basis of the correspondence in the ν_1 frequency of the species in solution and that of a solid, which had an empirical formula corresponding to $\text{Na}(\text{UO}_2)_2\text{CO}_3(\text{OH})_3$, that was isolated from the partial evaporation of a uranyl carbonate solution.⁶

It is seen that $\text{U}_2\text{O}_5\text{CO}_3\text{OH}^-$ as described by Blake et al.⁴ and $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ as assigned in this work are equivalent; this latter species will be referred to as the hemicarbonat.

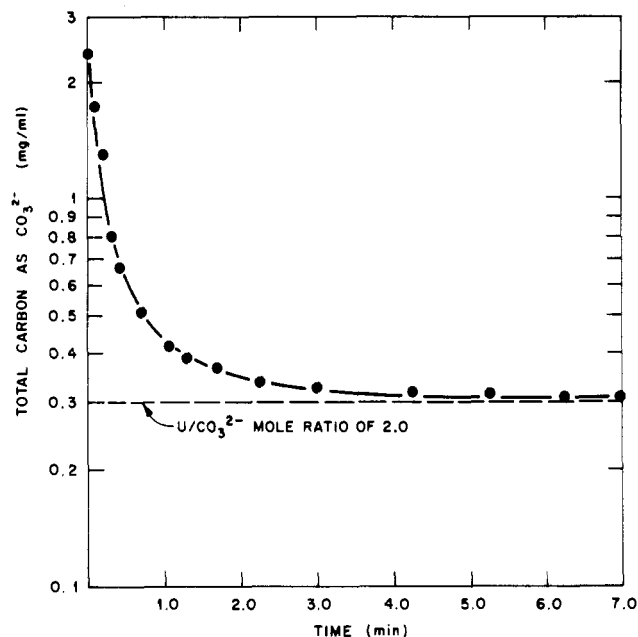


Figure 2. Rate of decrease in carbon content of a 0.01 M U solution while CO_2 is displaced with an inert gas passed at a constant rate.

The conversion of the free uranyl ion through hydrolysis, partial complexation, and up to the stage of complete carbonate complexation was followed by electrochemical means. The cyclic voltammogram of a 0.01 M uranyl nitrate solution in 0.1 M NaNO_3 at pH 3.4 showed three cathodic peaks at -0.2 , -0.82 , and -0.92 V vs. SCE. These measurements are in agreement with those made in perchlorate media.⁸ These peaks correspond respectively to the reduction of U(VI) to U(V), U(V) to U(IV), and U(IV) to U(III). At this point CO_2 was introduced into the system, and 2.5 equiv NaOH/equiv of U was added. The resulting solution (pH 5.0) showed a complex broad peak at -0.39 V with shoulders at -0.45 and -0.25 V . The cathodic peaks at -0.8 and -0.9 V disappeared at this point. The observed complexity of the broad peak reflects the multiplicity of species at that stage. A U material balance calculation of the composition of this solution shows $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and UO_2CO_3 as the major species present. Displacement of CO_2 from the system, which causes a concurrent increase in pH, altered the shape and position of the U(VI)–U(V) reduction peak. At pH 5.5 the peak was displaced to -0.5 V , and it showed a shoulder at -0.27 V . At pH 6.5 there was a considerable sharpening of the peak and displacement to -0.62 V although a shoulder at -0.5 V could still be observed. At pH 7.6 the shoulder disappeared without any additional displacement of the peak. At this point a NaHCO_3 solution was introduced in small increments. The pH remained constant at about pH 7.5. Throughout the addition of 4.0 equiv $\text{NaHCO}_3/\text{equiv}$ of U, the reduction process at -0.62 V showed a continuous decrease in current and completely disappeared at the end of the addition. On the other hand, a new peak appeared at -1.3 V that grew in proportion to the amount of bicarbonate added. The reduction process at -1.3 V corresponds to the conversion of $\text{UO}_2(\text{CO}_3)_3^{4-}$ into an unstable U(V) species.⁹

The electrochemical changes described above are interpreted as resulting from the transformation of $\text{UO}_2^{2+} \cdot x\text{H}_2\text{O}$ into a mixture of hydrolytic species as the pH increases in the presence of CO_2 to a value of 5.0. Further increments in pH cause the formation of hemicarbonat as the dominant species.

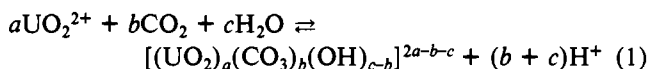
(6) L. Maya and G. M. Begun, *J. Inorg. Nucl. Chem.*, **43**, 2827 (1981).
 (7) L. M. Toth and G. M. Begun, *J. Phys. Chem.*, **85**, 547 (1981).

(8) L. Sipos, L. J. Jeftic, and M. Branica, *J. Electroanal. Chem. Interfacial Electrochem.*, **32**, 35 (1971).
 (9) D. W. Wester and J. C. Sullivan, *Inorg. Chem.*, **19**, 2838 (1980).

The decrease in current of the peak at -0.62 V, upon addition of HCO_3^- , and the corresponding increase of current of the peak at -1.3 V reflect the conversion of hem碳酸 into tricarbonat. The observations are consistent with the behavior of uranium solutions as followed by visible and Raman spectroscopy. This physical evidence together with the experiments establishing the stoichiometry of the species supports the assignment of $[(\text{UO}_2)_2\text{CO}_3(\text{OH})_3]_n$ as the formula of the species. The charge of the species was established by the acid or base demand required to reach that composition.

Stability Constant of Uranyl Hem碳酸. The stability constants of the species formed by the interaction of UO_2^{2+} , CO_2 , and H_2O as a function of pH were derived from the data collected in the course of potentiometric titrations. The initial uranium concentration of the solutions was 10^{-3} M (in one case 2×10^{-3} M). This rather narrow range was dictated by the properties of hem碳酸-rich solutions. These could be prepared at a total uranium concentration up to 0.002 M in 0.1 M NaClO_4 . Higher concentrations of background electrolyte promote solids formation near the neutral-pH range.

The stability constants calculated refer to the generalized equation



For simplicity we define $c-b = x$, $b+c = y$, and $2a-b-c = z$.

The stability constants of the species involved are then defined as

$$*\beta_{abx} = \frac{[abx^z][\text{H}^+]^y}{[\text{UO}_2^{2+}]^a p_{\text{CO}_2}^b} \quad (2)$$

The values of the stability constants were obtained by means of the nonlinear least-squares program ORGLS.¹⁰ This involved the solution of two functions defining the charge balance and the uranium mass balance

$$f(1) = [\text{H}^+] + 2[\text{UO}_2^{2+}] + [\text{Na}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] - [\text{ClO}_4^-] + \sum z\beta_{abx}[\text{UO}_2^{2+}]^a p_{\text{CO}_2}^b [\text{H}^+]^{-y}$$

$$f(2) = [\text{U}_t] - [\text{UO}_2^{2+}] - \sum a\beta_{abx}[\text{UO}_2^{2+}]^a p_{\text{CO}_2}^b [\text{H}^+]^{-y}$$

where U_t is the total uranium concentration.

Analysis of the data required a knowledge of the values of the dissociation constants of H_2CO_3 in the medium examined. A few titrations were conducted under different partial pressures of CO_2 . The results of these titrations were also analyzed by means of ORGLS. The values found were $-\log *K_1 = 7.73 \pm 0.004$ and $-\log K_2 = 9.95 \pm 0.03$. The $*K_1$ refers to the equilibrium $[\text{HCO}_3^-][\text{H}^+]p_{\text{CO}_2}^{-1}$; it is related to K_1 by the expression $*K_1 = K_H K_1$, where K_H is Henry's constant for the conditions examined.

A few typical results of the titration of the uranium solution are given in Table I. The complete data set comprised 70 data points. Plots of titrations under different CO_2 partial pressures are shown in Figure 3.

A statistical analysis of replicates within the data set showed standard deviations of about 0.015 pH unit for values preceding the inflection point in the titration plot and about 0.1 for values around that point. The data set was accordingly weighted in the course of the analysis. The average deviation for the data set was 0.042 pH unit.

The model considered for the data analysis was initially restricted to the following species: 2,0,2; 3,0,5; 2,1,3; 1,2,0; 1,3,0. The numbers represent values of a , b , and x as defined

Table I. Typical Data of Titration of 50 mL of Uranyl Tricarbonat-Sodium Bicarbonat, 0.001 M U and 0.0048 M Na, with 0.1 M HClO_4

$-\log [\text{H}^+]$	HClO_4 , mL	$-\log p_{\text{CO}_2}$	$-\log [\text{H}^+]$	HClO_4 , mL	$-\log p_{\text{CO}_2}$
8.414	0	3.550	8.411	0	3.543
8.357	0.45	3.550	8.364	0.45	3.543
8.304	0.90	3.550	8.292	0.90	3.543
8.207	1.30	3.550	8.218	1.30	3.543
8.030	1.75	3.550	7.982	1.75	3.543
6.815	2.20	3.550	6.633	2.20	3.543
6.029	2.45	3.550	5.970	2.45	3.543
5.053	2.70	3.550	4.985	2.70	3.543
7.648	0	2.554	7.174	0	2.024
7.601	0.45	2.554	7.105	0.45	2.024
7.563	0.70	2.554	7.062	0.70	2.024
7.505	0.95	2.554	7.006	0.95	2.024
7.445	1.20	2.554	6.866	1.40	2.024
7.345	1.45	2.554	6.667	1.70	2.024
7.181	1.70	2.554	6.352	1.95	2.024
6.880	1.95	2.554	5.715	2.20	2.024
6.127	2.20	2.554	5.339	2.45	2.024
5.640	2.45	2.554	4.865	2.70	2.024
4.940	2.70	2.554			

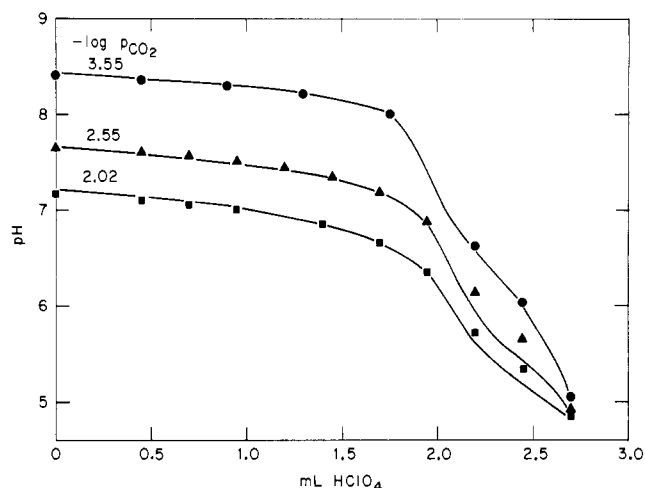


Figure 3. Typical titration plots of 50 mL of a 0.001 M U and 0.048 M Na solution with 0.1 M HClO_4 under different partial CO_2 pressures. Solid points denote experimental data; curves are calculated from a least-squares fit using species 1,0,0, 2,0,2, 3,0,5, 2,1,3, 1,2,0, 1,3,0, and 1,1,0. Numbers are values a , b , and x that define the stoichiometry of the species according to eq 2 in the text.

by eq 2. Additional species as well as alternates were introduced to improve the fit. The choice of species tested was based on other possible species reported in the literature. The species 11,6,12, 1,1,0, and 3,1,3 detected by Ciavatta et al.¹¹ in titrations of uranyl ion under different partial pressures of CO_2 , covering the acidic range up to pH 5.0, did not significantly contribute to the uranium species present in the pH and p_{CO_2} ranges covered in the present study.

The species 6,3,10 was also considered because of the existence of natural uranium minerals, the zippeites,¹² which have ligand ratios similar to the 2,1,3 species but contain SO_4^{2-} instead of CO_3^{2-} . This species made the fit worse when introduced as an alternate of 2,1,3 and produced no significant improvement when introduced in addition to 2,1,3. Similar results were obtained in testing the species 4,2,6, 4,2,7, and 1,1,1. The latter was proposed in combination with the species 3,0,7 by Tsymbal to account for an intermediate in the pH

(10) W. R. Busing and H. A. Levy, Report ORNL-TM-271, Oak Ridge National Laboratory, Oak Ridge, TN, 1962.

(11) L. Ciavatta, D. Ferri, M. Grimaldi, R. Palombi, and F. Salvatore, *J. Inorg. Nucl. Chem.*, **41**, 1175 (1979).
(12) T. J. O'Brien and P. A. Williams, *Inorg. Nucl. Chem. Lett.*, **17**, 105 (1981).

Table II. Stability Constants of Hydroxouranyl and (Carbonato)uranyl Species

species	this work		literature values		ref
	$-\log * \beta$	$\log \beta^a$	$-\log * \beta$	$\log \beta^a$	
1,3,0	31.21 ± 0.05	21.81	...	21.57	3
1,2,0	19.19 ± 0.29	16.15	...	16.16	3
2,1,3	18.63 ± 0.08		
3,0,5	16.19 ± 0.16		16.2		16
2,0,2	5.89 ± 0.37		5.8		16

^a Where $\log \beta_{130} = \log * \beta_{130} - 3 \log (*K_1 K_2)$ and $\log \beta_{120} = \log * \beta_{120} - 2 \log (*K_1 K_2)$. The K stands for the dissociation constants of H_2CO_3 .

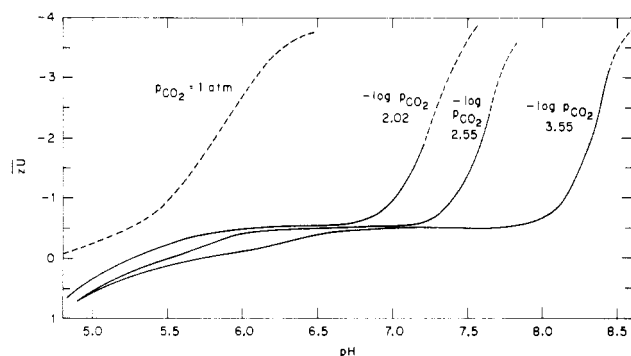


Figure 4. $\bar{z}(U)$ as a function of pH and p_{CO_2} at $a[U] = 0.001$ M. Solid lines describe conditions actually covered in this study. Dashed lines extend to calculated values.

range between complete complexation and complete hydrolysis. The values given by Tsymbal for the stability constants of these species are not consistent with the carbon content of uranium-carbonate solutions and the solubility data of β - $UO_3 \cdot H_2O$.¹³

Analysis of the data with the inclusion of additional hydrolytic species was also made. Testing a 4,0,7 species, proposed by Sylva et al.,¹⁴ gave no improvement. On the other hand, the species 3,0,7 improved the fit slightly, but inclusion of this species in the model was considered to be unjustified because its contribution becomes important at pH values of relatively large uncertainties.

Finally, the consideration was given to the species 3,6,0 as an alternate to 1,2,0. This species was reported recently by Ciavatta et al.¹⁵ on the basis of potentiometric and ¹³C NMR data, but no stability constant was given. Its introduction produced large uncertainties on its stability constant. This is apparently a result of the minor contribution of this species to the total uranium concentration in the p_{CO_2} range covered in the present study.

The final fit of the data was made with the species 1,3,0, 1,2,0, 2,1,3, 3,0,5, and 2,0,2. The values found for the stability constants of these species are given in Table II.

Mass balance as a function of pH and p_{CO_2} were used to calculate species distribution under different conditions. These are presented in a condensed manner in Figure 4. The curves represent the average charge on the uranium species, $\bar{z}(U)$, as a function of pH and p_{CO_2} . The values of $\bar{z}(U)$ are obtained from the expression

$$\bar{z}(U) = \frac{\sum z[abx^z]}{[U]}$$

(13) K. H. Gayer and H. Leider, *J. Am. Chem. Soc.*, **77**, 1448 (1955).

(14) R. N. Sylva and M. R. Davidson, *J. Chem. Soc., Dalton Trans.*, 465 (1979).

(15) L. Ciavatta, D. Ferri, I. Grenthe, and F. Salvatore, *Inorg. Chem.*, **20**, 463 (1981).

(16) C. F. Baes, Jr., and R. E. Mesmer, "The Hydrolysis of Cations", Wiley, New York, 1976.

There is a similarity between the $\bar{z}(U)$ vs. pH plots presented here and the more familiar \bar{n} vs. $[L]$ plots, where \bar{n} is the average ligand number and $[L]$ is the ligand concentration. The similarity is not coincidental since $[CO_3^{2-}]$ is implicit by a combination of the pH and p_{CO_2} values.

Figure 4 shows a few relations that describe the system. The flat portion of the plots roughly defines the conditions of predominance of the hemicarbonato species. The pH range of existence of this species decreases as p_{CO_2} increases and becomes quite limited at 1 atm of CO_2 . The steep rise in $\bar{z}(U)$ values occurring within a narrow pH range, particularly at low p_{CO_2} , is a reflection of the rather large difference, of the order of $10^{5.5}$, in the stability constants of the tricarbonato and dicarbonato complexes. The contribution of the hydrolytic species is evident in the pH range where the $\bar{z}(U)$ values approach zero and become positive.

Conclusions

The existence of a hydroxocarbonato species having a U/ CO_3 mole ratio of 2.0 has been demonstrated by analytical, spectroscopic, and electrochemical means. The stoichiometry of the reactions leading to its formation from either UO_2^{2+} or $UO_2(CO_3)_3^{4-}$ and the data analyses of the potentiometric titrations indicate that this species is apparently $(UO_2)_2CO_3(OH)_3^-$.

The set of equilibrium constants derived from the fit of the data is in good agreement with values in the literature for those species that are known, therefore lending support to the reliability of the constant derived for the formation of the hemicarbonato species.

The hemicarbonato species is of importance under conditions similar to those found in natural waters, and it should be considered in speciation schemes of uranium(VI) in nature.

An integrated view of the carbonate complexation and hydrolysis of the uranyl ion as a function of pH and p_{CO_2} has been obtained.

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Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Preparation and Characterization of (μ -Dichloroboryl)pentaborane(9)

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A variety of pentaborane(9) derivatives with the general formula $(\mu-X_nM)_B_5H_8$ have been reported in the literature.^{1,2} In these compounds the substituent group MX_n is located at a basal bridge position of the pyramidal pentaborane framework. Among those reported, (μ -dimethylboryl)pentaborane(9) ($[\mu-(CH_3)_2B]B_5H_8$) is unique in that the boron atom at the bridge position, or the B in the $B(CH_3)_2$ group, is sp^2 hybridized and the p_z orbital is left unused.³

(1) Gaines, D. F. *Acc. Chem. Res.* **1973**, *6*, 416 and references therein.

(2) Gaines, D. F. In "Boron Chemistry-4"; Parry, R. W., Kodama, G., Eds.; Pergamon Press: Elmsford, NY, 1980; p 73 and references therein.

(3) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1970**, *92*, 4571.