Table II. Comparisons of the Photochemical Quantum Yields for Loss of L from $(CN)_5ML^{n-}$

L	Φ_L, mol/einstein M = Co(III)[a]	 M = Fe(II)[b]
pyridine	0.17 ± 0.02 (3)	0.23
3,5-dichloropyridine	0.40 ± 0.02 (5)	
isonicotinamide	0.12 ± 0.01 (4)	0.41
pyrazine	0.24 ± 0.02 (6)	0.39
4-cyanopyridine	0.14 ± 0.01 (5)	0.30
N-methylpyrazinium	0.22 ± 0.02 (4)	0.022[c]

[a] Initial quantum yield and average deviation with number of determinations in parentheses ($\overline{\nu}_{irr} = 2.74\ \mu m^{-1}$). [b] Initial quantum yield from ref 2. [c] For irradiation of $2.29\ \mu m^{-1}$.

$2.92\ \mu m^{-1}$ (342 nm), but absorption in this region is intensified by the low-energy tailing of an internal ligand band.) The insensitivity of the maximum of the lowest energy, spin-allowed, absorption band to changes in L is characteristic of the LF nature of this transition (see also rhodium(III) ammine homologues[3]) but differs from the isoelectronic $(CN)_5Fe^{II}L^{(n+1)-}$[2] and analogous $(NH_3)_5RuL^{n+}$[3] and $(CO)_5WL$[5] systems where this absorption band is MLCT in nature and extremely sensitive to changes in L. For discussion purposes, the cobalt compounds are listed in Table II by descending order of the MLCT maxima energies for the isoelectronic $(CN)_5Fe^{II}L^{(n+1)-}$ complexes.[2]

Quantum Yield Determinations. Irradiation of air-saturated or deoxygenated, aqueous solutions (pH 7, $[(CN)_5Co^{III}L] = (2 \pm 1) \times 10^{-3}$ M) leads to the photoaquation of L with initial quantum yields as reported in Table II. Thermal control studies show that over the time span of the photolysis experiment, generally 0.5–2 h, no degradation of the dark solution is observed. The photolyzed sample undergoes a continuous spectral change from $(CN)_5Co^{III}L^{n-}$ to $(CN)_5Co^{III}OH_2^{2-}$ with isosbestic points maintained throughout the entire photodecomposition. The final absorption spectrum of extensively irradiated solutions corresponds exactly to a spectrum of authentic $(CN)_5Co^{III}OH_2^{2-}$ with the calculated concentration of Co(III) showing excellent agreement with the gravimetric concentration of the starting compound, $(CN)_5Co^{III}L^{n-}$. These results coupled with the atomic absorption studies on $K_x[(CN)_5Co^{III}L]\cdot xH_2O$ indicate that the initial complexes are pure and that extensive photolysis of $(CN)_5Co^{III}L^{n-}$ leads solely to $(CN)_5Co^{III}OH_2^{2-}$.

Comparison to the Isoelectronic Fe(II) System. Quantum yields for the photoaquation of L from $(CN)_5Co^{III}L^{n-}$ in this work and the previously reported[2] $(CN)_5Fe^{II}L^{(n+1)-}$ complexes are reported in Table II. The choice of various ligands in the study encompasses isoelectronic Fe(II) compounds which are photochemically reactive[2] (i.e., ^{3}LF state presumed lower in energy than MLCT; L = pyridine, isonicotinamide, pyrazine, and 4-cyanopyridine) and photochemically nonreactive[2] (i.e., MLCT state presumed lower in energy than ^{3}LF; L = *N*-methylpyrazinium). We observe substantial substitutional reactivity ($\Phi_L > 0.1$) for all of the Co(III) compounds in this study. This suggests that the drop-off in quantum yield in the Fe(II) sequence when L = *N*-methylpyrazinium is not anomalous ligand behavior but is due to a crossover of LF and MLCT states as previously postulated.[2]

A comparison of the quantum yields for the isoelectronic $(CN)_5Fe^{II}$ and $(CN)_5Co^{III}$ systems for L in which LF reactivity is observed for both metal centers (i.e., L ≠ *N*-methylpyrazinum) shows one interesting correlation. In all such choices of L, the Co(III) quantum yield is smaller than the analogous Fe(II) quantum yield. This may reflect a greater difficulty in breaking the M–L bond in the excited state of the 2– charged $(CN)_5Co^{III}$ metal center than in the 3– charged $(CN)_5Fe^{II}$. This explanation is consistent with electrostatic considerations of removing a nitrogen base from the metal center and parallels, but is less dramatic than, the relative ground-state substitutional reactivity (from ref 2 and this work). However, any direct comparison of Fe(II) and Co(III) quantum yields relies on the unlikely assumption that the lifetimes of the Co(III) and Fe(II) excited states (and thus the nonradiative decay rates) are similar for the two compounds.

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Registry No. $K_2[(CN)_5CoL]$ (L = pyridine), 14706-00-4; $K_2[(CN)_5CoL]$ (L = 3,5-dichloropyridine), 74312-83-7; $K_2[(CN)_5CoL]$ (L = isonicotinamide), 74312-84-8; $K_2[(CN)_5CoL]$ (L = pyrazine), 74312-85-9; $K_2[(CN)_5CoL]$ (L = 4-cyanopyridine), 74345-92-9; $K[(CN)_5CoL]$ (L = *N*-methylpyrazinium), 74312-86-0.

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Electrochemical and Spectroscopic Studies of Uranium(IV), -(V), and -(VI) in Carbonate–Bicarbonate Buffers[1]

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Disproportionation of uranium(V) produced electrochemically by reduction of uranyl ion in bicarbonate solutions was reported by Brancia and Pravdic.[2] Stabilization of U(V) in carbonate solutions with pH >11 was observed by these and other workers.[3-5] In each case the U(V)–carbonate solution was observed to be colorless. Spectroscopic studies[6,7] of uranyl ion in carbonate and bicarbonate media indicate that the $UO_2(CO_3)_3^{4-}$ ion is formed in both solutions. Recently a need for more detailed knowledge of the chemistry of actinide ions in basic media has arisen in connection with deducing their chemistry in the environment. In this work we report the results of polarographic, cyclic voltammetric, and spectroscopic studies of U(IV), -(V), and -(VI) in carbonate and bicarbonate media. Polarographic studies were in excellent agreement with those reported previously.[2] Cyclic voltammetric scans confirmed the irreversible reduction to U(V) in both solutions, but disproportionation of the U(V) was observed only in the bicarbonate solutions. The oxidation of U(V) in carbonate was followed spectroscopically for the first time. Reduction in bicarbonate produced U(IV), the spectrum of which is now reported and the oxidation of which was also followed spectroscopically for the first time.

Experimental Section

Anhydrous powdered Na_2CO_3 (analytical reagent, Mallinckrodt, St. Louis, MO, and ultrapure, Alfa Products, Danvers, MA), certified $NaHCO_3$ (Fisher Scientific Co., Fair Lawn, NJ), and $UO_2(ClO_4)_2$ (Research Organic/Inorganic Chemical Corp., Sun Valley, CA) were used as received. Solutions were prepared by using triply distilled

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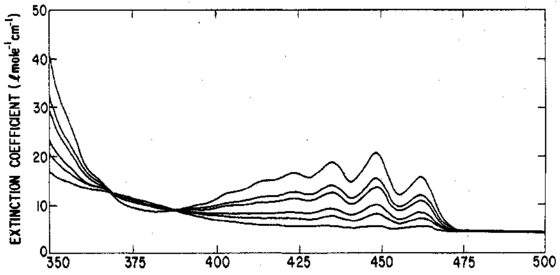

Figure 1. Oxidation by air of U(V) (0.01 M) in Na_2CO_3 (1 M) as followed in the visible spectrum. Isosbetic points occur at 368 and 388 nm. The absorbance from 388 to 475 nm increases as the oxidation proceeds.

water. Degassing of solutions with water-saturated, deoxygenated (chromous chloride) nitrogen preceded all measurements except where explicitly stated.

Polarograms were obtained by using a Princeton Applied Research (PAR) Model 174A polarographic analyzer and drop timer. Cyclic voltammograms were obtained by using a PAR Model 173 potentiostat galvanostat driven by a PAR Model 175 universal programmer. Recording was done on a PAR Model 9002A X-Y recorder or Tektronix Type RM564 storage oscilloscope. Controlled-potential coulometric data were taken from a PAR Model 179 digital coulometer.

Electrochemical cells used a three electrode systrem: a working electrode, platinum-wire counterelectrode, and saturated calomel (SCE) reference electrode. For the polarographic dropping-mercury electrode, triply distilled mercury flowed through a capillary, and drops were dislodged at regular intervals by a drop timer. A hanging-mercury-drop electrode was used for cyclic voltammetry. A mercury-pool electrode was used for controlled potential coulometry. Platinum wire was rinsed with distilled water and flamed prior to use. The reference electrode was separated from the bulk of the solution by a bridge having Vycor frits and containing blank electrolyte. All voltages reported in this work are vs. the SCE. Cells were thermostated at 25 °C by using a Haake FK circulator. Visible spectra were recorded on a Cary 14 recording spectrophotometer.

Results and Discussion

Carbonate Solutions. Polarograms of carbonate solutions (0.1–1 M Na_2CO_3) containing 10^{-2} M UO_2^{2+} show a single reduction wave at ca. −0.95 V. As was found previously,[2] the wave represents a one-electron reduction and is irreversible. Our polarograms gave excellent agreement with these earlier observations. Cyclic voltammograms of ca. 10^{-2} M UO_2^{2+} in 0.1–1 M Na_2CO_3 solutions showed behavior identical with that reported previously.[5]

Controlled-potential reduction at −1.2 V of 10^{-2} M UO_2^{2+} in 1 M sodium carbonate gave an average value of 1.02 ± 0.04 electrons per uranium atom. The reduction of the solution was accompanied by a color change from yellow to colorless. Cyclic voltammograms of the U(V) solution showed oxidation and reduction waves at the same voltages as those of the U(VI) solution. However, the anodic peak current was larger than the cathodic current.

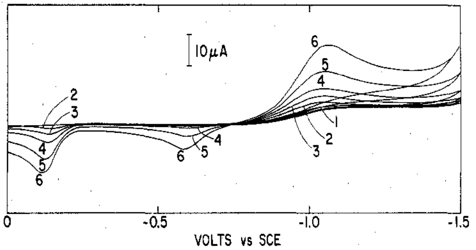

Figure 2. Cyclic voltammograms of $UO_2(ClO_4)_2$ (0.01 M) in $NaHCO_3$ (1 M). Scan rate values (mV/s) are (1) 2, (2) 5, (3) 10, (4) 20, (5) 50, (6) 100.

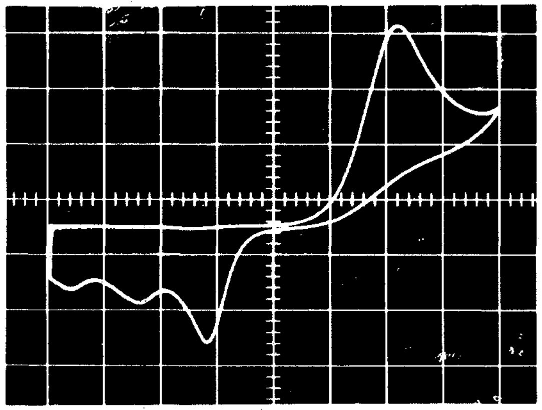

Figure 3. Cyclic voltammogram of $UO_2(ClO_4)_2$ (0.01 M) in $NaHCO_3$ (1 M) at 2 V/s from 0.0 to −1.5 vs. SCE. The current scale is in arbitrary units.

The visible spectrum of the U(V) solution is virtually featureless at this concentration. A shoulder at 365 nm is the main feature of the spectrum. The spectra of U(V) in 1 M K_2CO_3 from 650–1350 nm,[3] in molten LiCl–$MgCl_2$ from 400–2000 nm,[3] and in dilute acid[8] have been reported. Due to the much lower concentrations used in this study and the very small extinction coefficients, we were unable to observe the structure from 650–1350 nm, as observed previously. Colorless solutions of U(V) in 1 M K_2CO_3 have also been noted;[3] however, the spectrum in the visible region was not reported.

Reactions of U(V) with several oxidizing agents were observed spectrophotometrically. Figure 1 shows the oxidation by air of 0.01 M U(V) in 1 M Na_2CO_3 solution. As the oxidation proceeds, the featureless U(V) spectrum changes to the spectrum of UO_2^{2+} in carbonate media.[6] The appearance of isosbestic points at 368 and 388 nm is consistent with one reactant producing a single product. At these concentrations of carbonate and uranium, the predominant product is $UO_2(CO_3)_3^{4-}$. Kinetic studies utilizing U(V) as a 1-equiv reductant in basic media are in progress.

Bicarbonate Solutions. Polarograms of bicarbonate solutions (0.1 M $NaHCO_3$) of UO_2^{2+} (0.01 M) show one reduction wave at −1.22 V. The wave represents an irreversible one-electron reduction. The product of this reduction, presumably a U(V) species, is unstable with respect to disproportionation and will be discussed below.

Cyclic voltammograms (Figures 2 and 3) of UO_2^{2+} (0.1 M) in sodium bicarbonate solution (1 M) show dramatic changes as a function of scan rate. At the slowest scan rates (2–100 mV/s), a cathodic peak (ca. −1.05 V) and two anodic peaks (ca. −0.12 and −0.50 V) are observed. As the scan rate is increased, the anodic peak current at ca. −0.12 V grows more slowly than that at ca. −0.50 V. The cyclic voltammograms at scan rates >10 V/s show only a cathodic peak at ca. −1.27 V and an anodic peak at ca. −0.47 V. A third anodic peak at ca. −0.30 V is observed at scan rates of 1–10 V/s (Figure 3).

The cyclic voltammograms are interpreted in terms of the mechanism of disproportionation proposed previously.[2] The cathodic wave can be interpreted as a one-electron reduction of $UO_2(CO_3)_3^{4-}$ to produce the U(V) species. However, this product of electroreduction quickly disproportionates in 1 M $NaHCO_3$ to produce U(IV) and U(VI) species. Thus, anodic peaks at ca. −0.12 and −0.50 V corresponding to the oxidation of U(IV) and U(V), respectively, are observed at the slower

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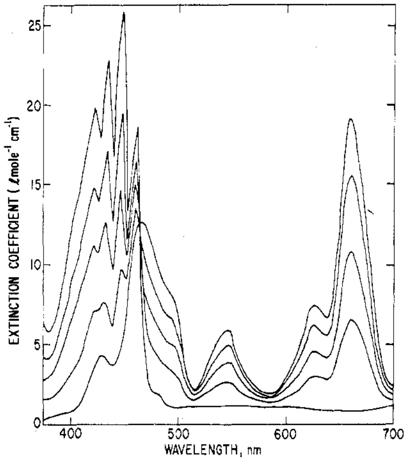

Figure 4. Oxidation by air of U(IV) (0.02 M) in $NaHCO_3$ (1 M) as followed in the visible spectrum. An isosbestic point occurs at 465 nm. Absorbance less than 465 nm increases as the oxidation proceeds, while absorbance greater than 465 nm decreases.

scan rates. The U(IV) peak current is greater than that for U(V) since the disproportionation reaction is completed. As the scan rate is increased, the anodic scan is completed before the disproportionation reaction proceeds to any great extent. Thus, an anodic peak at ca. −0.47 V corresponding to oxidation of U(V) is the only feature at the fastest scan rates. The anodic peak at ca. −0.30 V, which occurs between the two major peaks, is ascribed to the oxidation of an intermediate species. From studies in carbonate media, the anodic wave corresponding to oxidation of U(V) is known to occur at ca. −0.50 V, i.e., the wave seen at the fastest scan rates. At slower scan rates, disproportionation has produced some intermediate, the oxidation wave of which is postulated to occur at ca. −0.30 V. However, at the same scan rates at which the intermediate is first observed, the oxidation wave of U(IV) also appears. Thus, the intermediate that is produced quickly undergoes disproportionation while U(V) may exist for a time that is relatively long compared to the lifetime of the intermediate.

Controlled-potential reduction at −1.25 V of 0.01 M UO_2^{2+} in 1 M $NaHCO_3$ solution gives an average value of 2.00 ± 0.03 electrons for each uranium. Reduction of the solution is accompanied by a color change from yellow to pale brownish yellow. Cyclic voltammograms of the reduced solution show a cathodic wave at ca. −1.05 V and an anodic wave at ca. 0.12 V. It is interesting to note that repetitive scans of the reduced solution indicate a buildup of both U(VI) and U(V) in the diffusion layer.

The visible spectrum of the reduced solution is similar to that of U(IV) in carbonate.[4] Comparison with previously reported spectra of $U(CO_3)_x^{(4-2x)+}$ complexes,[10] U(IV) polymeric solutions,[11] and a $U(OH)^{3+}$ spectrum[12] shows a remarkable degree of similarity in view of the widely differing systems. The major peaks (with extinction coefficients in parentheses) are located at 430 (4.45), 466 (12.8), 495 (sh, 8.25), 547 (5.85), 625 (7.45), and 660 (19.1) nm. The solution follows Beer's law over the concentration range 0.02–0.001 M.

Figure 4 shows the changes in the visible spectrum as U(IV) in bicarbonate is oxidized by air. The initial U(IV) spectrum gradually changes to that of $UO_2(CO_3)_3^{4-}$. An isosbestic point occurs at 465 nm. The occurrence of the isosbestic point is consistent with the oxidation proceeding to only one product. Therefore, the U(IV) species may prove to be an excellent 2-equiv reductant in basic solution.

Chemical synthesis of the U(IV)-bicarbonate species is readily accomplished by dissolving UCl_4 in 1 M $NaHCO_3$. Addition of solid UCl_4 to 1 M $NaHCO_3$ leads initially to a greenish precipitate which readily dissolves on gentle heating. Cyclic voltammograms and visible spectra of this solution are identical with those of solutions produced by electrochemical reduction of UO_2^{2+} in 1 M $NaHCO_3$.

Registry No. $UO_2(ClO_4)_2$, 13093-00-0; U, 7440-61-1.

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Technetium Radiopharmaceutical Development. 2. Preparation, Characterization, and Synthetic Utility of the Oxotetrahalotechnetate(V) Species $TcOX_4^-$

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and Edward Deutsch*[1]

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The preeminence of ^{99m}Tc in diagnostic nuclear medicine has led to considerable interest in developing the nascent inorganic chemistry of technetium.[3] To this end our research groups have recently prepared and characterized the complexes $TcOCl_4^-$[4] and $TcHBPz_3Cl_2O$[5] ($HBPz_3^-$ = hydrotris(1-pyrazolyl)borate anion) utilizing the long-lived ^{99}Tc isotope. We have now extended this work to include the bromo analogues $TcOBr_4^-$ and $TcHBPz_3Br_2O$. It appears that $TcOX_4^-$ anions are probable intermediates in the preparation of the poly(1-pyrazolyl)borate complexes, and we have thus focused our attention on these oxotetrahalotechnetate(V) anions as valuable synthetic starting materials for the development of technetium radiopharmaceuticals.

Experimental Section

General Data. All common laboratory chemicals were of reagent grade. The $NH_4{}^{99}TcO_4$, containing technetium-99 of >99% radiochemical purity, was obtained from Oak Ridge National Laboratories, Oak Ridge, TN. $K^{99}TcO_4$ was made from NH_4TcO_4 by metathesis with KOH and was twice recrystallized from water. Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, TN. Hexane and dichloromethane were dried over 3-Å molecular sieves for 1 week prior to use. Visible–UV spectra were recorded on a Varian 634 spectrophotometer at ambient temperature in dichloromethane. Mass spectra were obtained by using a RMU-7 instrument at 50 eV and 50 °C. ^1H NMR spectra were obtained with a Varian T-60 instrument in acetone-d_6 (internal Me_4Si reference). IR spectra were recorded on a Perkin-Elmer 599 in Nujol mulls and KBr pellets. The laser Raman spectrum was obtained in the solid state through the courtesy of Dr. J. E. Smith, Union Carbide Corp., Tarrytown, NY.

Tetrabutylammonium Oxotetrabromotechnetate(V), $[(n\text{-}Bu)_4N]TcOBr_4$. To 43.0 mg of $KTcO_4$ held at 0 °C in a 10-mL beaker was added 2.0 mL of 48% HBr at ambient temperature. The resulting mixture was stirred at 0 °C, and as the $KTcO_4$ dissolved, the mixture

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