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OXYGEN-17 NMR STUDIES OF URANIUM (VI) HYDROLYSIS AND GELATION

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ABSTRACT

Hydrolysis and gelation processes in uranyl solutions are observed using the strong sharp oxygen-17 resonance.

INTRODUCTION

The hydrolysis and subsequent gelation of uranyl ion is of both fundamental and practical interest. From a fundamental point of view the uranyl and other actinyl ions are unusual in having inert strong multiple bonds to the axial oxygen atoms and labile weak bonds to the equatorial ligands. From a practical point of view the hydrolysis and subsequent gelation of uranyl ion is important in connection with the manufacture of UO_2 microspheres for nuclear fuel applications [1].

This paper describes our efforts to follow the hydrolysis and gelation of uranyl derivatives by using oxygen-17 NMR spectroscopy of the axial oxygens as a probe. The oxygen-17 resonance of the axial uranyl oxygens, which was first observed by Rabideau [2], is very narrow and thus very easy to observe relative to other types of resonances of the quadrupolar oxygen-17 nucleus. In addition the position of the oxygen resonance in uranyl derivatives is very sensitive to the equatorial ligands [3] and even to isotopic substitution of the opposite uranyl oxygen atom [4]. Furthermore the kinetic inertness of the axial uranyl oxygen to oxygen exchange [5] allows distinct resonances for different types of uranyl groups to be observed in mixtures of uranyl species rather than a single uranyl resonance at an average chemical shift for the components of the mixture.

EXPERIMENTAL

Oxygen-17 NMR spectra were obtained at 11.7T (67.8 MHz) on a Bruker AM-500 at the Chemistry Department of the University of South Carolina. Data were acquired at a sweep width of 125 kHz following excitation by a 6.2 msec pulse ($\sim 66^\circ$). Each scan consisted of 65,536 (64K) data points. Minimum relaxation delays were used giving a 0.262 sec recycle time. The resulting FID's were zero filled to 128K before transformation yielding a digital resolution of 1.9 Hz/point. The spectra in the Figures are the sum of 4096 individual scans. Chemical shifts are reported relative to H_2O and were referenced to an external $\text{D}_2\text{O}/\text{H}_2\text{O}$ standard. All samples were run in 5 mm NMR tubes and spectra were acquired at ambient temperature. Concentrated (1.8 to 3.9 M) aqueous stock solutions of uranyl chloride and uranyl nitrate were enriched photolytically [5] to 5 to 10% oxygen-17 using commercial 28% enriched oxygen-17 water purchased from Icon Services, Inc. (Summit, New Jersey).

RESULTS

Figure 1 shows the oxygen-17 NMR spectra in the uranyl region obtained by the hydrolysis of uranyl chloride by the addition of 10% aqueous Me_4NOH in 0.25 $\text{OH}^-/\text{UO}_2^{2+}$ increments. The final spectra clearly show the monomer, the dimer $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and the trimer $(\text{UO}_2)_3(\text{OH})_5^+$ at approximately 1119.4, 1121.2, and 1127.7 ppm, respectively. These assignments are consistent with the increases and decreases in peak intensities upon additions of successive increments of base. Similar spectra were obtained in an analogous hydrolysis of uranyl chloride using extraction with increments of a 0.5 M solution of tri-n-decylamine in xylene as the base [6]. Analogous hydrolysis experiments using uranyl nitrate

rather than uranyl chloride resulted in the production of less trimer and led to broader resonances indicating a significant dependence of the course of hydrolysis on the counteranion.

A question of interest is whether this hydrolysis pattern would be modified if a base was selected to promote gelation. In this connection hexamethylenetetramine, $(\text{CH}_2)_6\text{N}_4$ (HMTA), was selected as a base in view of its role as a gelation agent in the internal gelation process for the production of UO_2 microspheres [1]. Figure 2 shows the oxygen-17 NMR in the uranyl region obtained by hydrolysis of uranyl chloride by the incremental addition of aqueous HMTA. The hydrolysis pathway using HMTA (Figure 2) is seen to differ markedly from that using Me_4NOH (Figure 1) or amine extraction by leading selectively to production of trimer at HMTA/ UO_2^{2+} ratios above 0.6. If the hydrolysis of uranyl chloride is carried out by adding increments of an equimolar HMTA/urea mixture, thus more closely approximating the conditions of the internal gelation process [1], a series of uranyl oxygen-17 NMR spectra essential identical to that in Figure 2 is obtained indicating that addition of urea in such quantities does not have a significant effect on the uranyl hydrolysis by HMTA. If the hydrolysis of uranyl chloride with an equimolar HMTA/urea mixture was carried out to a base/ UO_2^{2+} ratio of 1/1 and the resulting NMR sample is allowed to stand overnight at ambient temperature, the solution became a gel. The oxygen-17 NMR spectrum of the gel was essentially identical to that of the same sample before gelation indicating that no significant change had taken place during the gelation process.

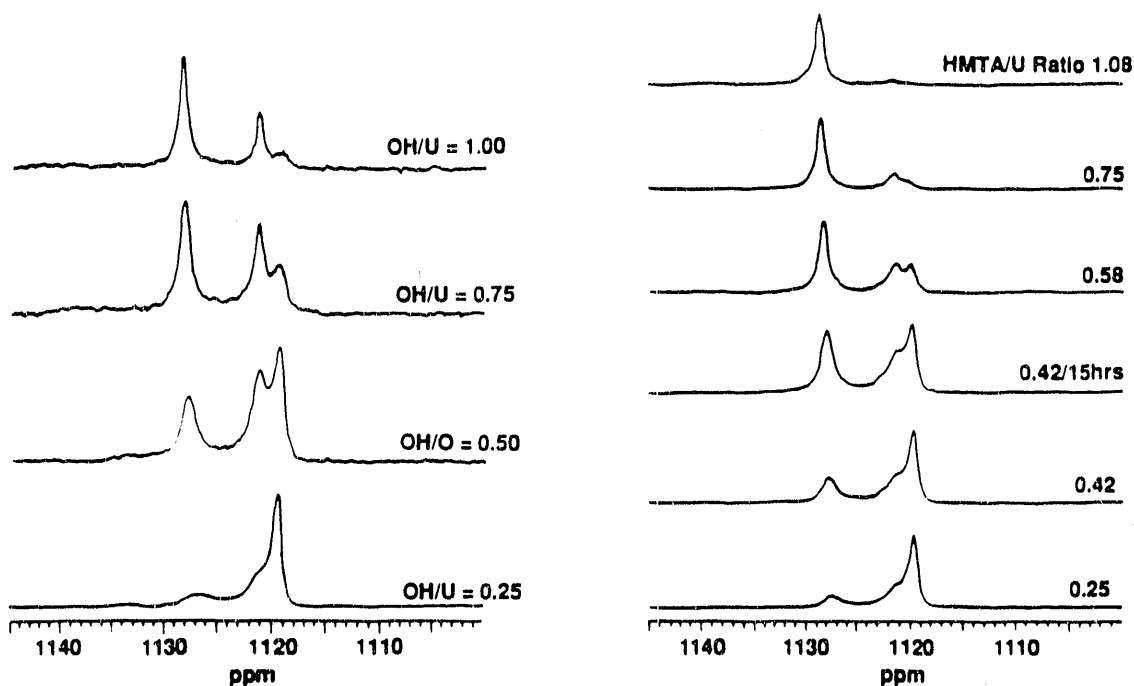


Figure 1. Oxygen-17 NMR spectra in the uranyl region of solutions obtained from the hydrolysis of 0.9M UO_2Cl_2 by addition of increments of 10% aqueous tetramethylammonium hydroxide

Figure 2. Oxygen-17 NMR spectra in the uranyl region of solutions obtained from the hydrolysis of 0.9M UO_2Cl_2 by addition of increments of 3M aqueous HMTA. This experiment was interrupted overnight when the HMTA/ UO_2 ratio was 0.42.

Gelation of a uranyl system was also studied in a strongly alkaline medium making use of the reported [7] appreciable solubility of actinyl salts in aqueous Me_4NOH . Photolysis of an approximately 0.1 M yellow solution of uranyl nitrate in 10% aqueous Me_4NOH ($\text{OH}^-/\text{UO}_2^{2+} = 9$) caused gelation. The oxygen-17 NMR spectrum of this gel exhibited a sharp resonance at 1114.4 ppm indicating directly for the first time the stability of the uranyl ion in strongly alkaline media in accord with reported [8] potentiometric and spectrometric studies.

DISCUSSION

The ability to follow the hydrolysis of uranyl salts by observation of the sharp uranyl oxygen-17 resonance provides a clear indication of the dependence of uranyl hydrolysis on the counteranion (nitrate versus chloride) but not on the means of introducing hydroxide into the solution (Me_4NOH versus R_3N extraction). In addition, two different pathways for gelation are suggested. In the first pathway the uranyl hydrolysis is conducted with a base (HMTA in these studies) which preferentially forms trimeric $(\text{UO}_2)_3(\mu_3\text{-O})$ units which can then condense into the polymeric $\text{UO}_2\text{O}_{6/3}$ layers of a gel based on the hexagonal structure of $\alpha\text{-UO}_2(\text{OH})_2$ [9]. In the second gelation pathway a uranyl derivative is treated with excess hydroxide in the absence of a metal or hydrogen-bonding ammonium cations which form insoluble solids uranates. Condensation of the resulting solution of soluble $\text{UO}_2(\text{OH})_n^{2-n}$ anions can then lead to a similar polymer $\text{UO}_2\text{O}_{4/2}$ or $\text{UO}_2\text{O}_{6/3}$ structure of a gel.

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