

The First Identification of Hydrolysis Species of Uranyl Ions by ^{17}O N.M.R. Spectroscopy

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The main hydrolysis species of uranyl ions, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$ and $[(\text{UO}_2)_3(\text{OH})_5]^+$, were identified by ^{17}O n.m.r. spectroscopy, signals being observed at 2.0 and 6.7 p.p.m. relative to the uranyl ion, respectively.

In a previous paper,¹ we explained why the oxygen atoms in the uranyl ion (uranyl oxygens) do not give a single ^{17}O resonance signal in strongly acidic solution. This is due not to the formation of hydrolysis species of the uranyl ion² but to oxygen isotope effects in the ^{17}O magnetic shielding of the

uranyl oxygens. The electronic structure of the hydrolysis species of the uranyl ion has been studied by various spectroscopic methods.³⁻⁵ The ^{17}O resonance of the uranyl oxygens has two characteristic aspects: i, the ^{17}O relaxation time is significantly long;⁶ ii, the ^{17}O chemical shift is very

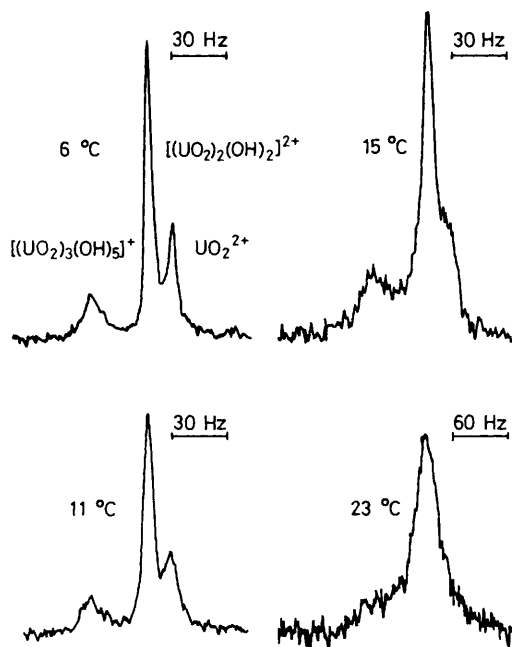


Figure 1. Changes in the ^{17}O n.m.r. spectrum of a uranyl solution with temperature: $[\text{UO}_2^{2+}]_t = 0.30 \text{ M}$ and $-\log[\text{H}^+] = 3.73$ at 6°C . Typical settings for the measurements are as follows: 8 K data points, 90° pulse angle corresponding to ca. $10 \mu\text{s}$ pulse width, 4 000 Hz spectral width, and normally 2 000 scans.

sensitive to changes in the equatorial ligand of UO_2^{2+} .⁷ Keeping these in mind, we investigated the potential of ^{17}O n.m.r. spectroscopy as a tool for studying these species.

We measured the ^{17}O n.m.r. spectra of ^{17}O -enriched uranyl ions¹ in nitrate solution, the acidity of the samples being adjusted with either NaOH or HNO_3 solution. ^{17}O N.m.r. spectra were recorded at 13.46 MHz on a JEOL JNM-FX 100 F.T.-n.m.r. spectrometer equipped with a JNM-VT-3B temperature controller. Under strongly acidic conditions there are no oxygen isotope effects in the ^{17}O magnetic shielding of the uranyl oxygens,¹ which give a single resonance, corresponding to $[\text{U}^{16}\text{O}=\text{U}^{17}\text{O}]^{2+}$, at ca. 1118 p.p.m. relative to pure water at room temperature. The linewidth remains almost constant (ca. 1 Hz) irrespective of acid concentration. In weakly acidic solution, however, the linewidth increases with decreasing acid concentration, and the spectra vary with temperature and the concentrations of UO_2^{2+} and H^+ in this acidic region.

Figure 1 shows the ^{17}O spectra of a uranyl solution for which $[\text{UO}_2^{2+}]_t = 0.30 \text{ M}$ ($t = \text{total}$) and $-\log[\text{H}^+] = 3.73$ at 6°C . Two extra ^{17}O resonances were observed to low field of the uranyl oxygens at the lower temperatures, at 2.0 and 6.7 p.p.m. relative to the uranyl ion at 6°C . The fact that the three resonances coalesce with increasing temperature indicates the occurrence of chemical exchanges among three species. The main hydrolysis species in the aqueous solution measured are $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$ and $[(\text{UO}_2)_3(\text{OH})_5]^+$,⁸ and the correlation time for ^{17}O quadrupolar relaxation of uranyl oxygens in the

latter trinuclear species, which is bulkier than UO_2^{2+} and $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$,⁸ is expected to be longer than those of these two species, leading to a broader linewidth. Therefore, the ^{17}O resonance observed at the lowest field can be assigned to $[(\text{UO}_2)_3(\text{OH})_5]^+$ and the middle line to $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$. In order to confirm the assignment, we measured the ratio of the relative intensities of the three species from Figure 1; $I_{1,0}:I_{2,2}:I_{3,5}^\dagger$ was 1.00:1.92:0.445 at 6°C . From this ratio, the concentrations of the three species $C_{1,0}$, $C_{2,2}$, and $C_{3,5}^\dagger$ were calculated as 0.089, 0.086, and 0.013 M, respectively. Equilibrium quotients of $Q_{2,2}$ and $Q_{3,5}$ were estimated to be $3.7 \times 10^{-7} \text{ M}$ and $4.2 \times 10^{-17} \text{ M}^3$, respectively. These values are close to the equilibrium quotients at 6°C calculated on the basis of thermodynamic parameters reported by Baes and Meyer,⁹ and lend support to our assignment. We could not observe ^{17}O resonances of bridged hydroxy ions in the hydrolysis species, presumably because the resonances are very broad or obscured by the ^{17}O resonance of water.

The electronic absorption bands corresponding to the $\text{O}' \rightarrow \text{O}''$ transition for the di- and tri-nuclear hydrolysis species have their maxima at longer wavelengths than that for UO_2^{2+} ,⁵ and the symmetric stretching frequencies for the hydrolysis species are lower than that for UO_2^{2+} because of the ligation of hydroxy ions.⁴ In view of the fact that ^{17}O chemical shifts of uranyl complexes increase when their lowest electronic transition energies are reduced by ligation,⁷ it is reasonable to expect $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$ and $[(\text{UO}_2)_3(\text{OH})_5]^+$ to show resonances to low field of UO_2^{2+} .

Assuming that the observed broadening in the ^{17}O resonance of UO_2^{2+} is attributed to an association reaction between UO_2^{2+} and $[\text{UO}_2\text{OH}]^+$,^{10,11} the second-order rate constant was estimated to be $1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 6°C .

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$\dagger I_{x,y}$ and $C_{x,y}$ refer to the relative intensity and the concentration of $[(\text{UO}_2)_x(\text{OH})_y]^{(2x-y)+}$, respectively.