Oxygen Isotope Shifts in ^{17}O NMR Spectra of the Uranyl Ion

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Synopsis. The ^{17}O NMR spectrum of uranyl oxygens enriched with ^{17}O gave three peaks. These peaks are assigned to the signals of three isotopomers, $[^{16}O=U=^{17}O]^{2+}$, $[^{17}O=U=^{17}O]^{2+}$, and $[^{18}O=U=^{17}O]^{2+}$. Chemical shifts for the signals of $[^{17}O=U=^{17}O]^{2+}$ and $[^{18}O=U=^{17}O]^{2+}$ were -0.054 ± 0.002 and -0.108 ± 0.002 ppm relative to $[^{16}O=U=^{17}O]^{2+}$, respectively.

The study of ^{17}O NMR spectra of oxygen in a dioxouranium(VI) ion, where hereafter uranyl oxygens will be used, was first reported by Rabideau.[1] He observed an asymmetric ^{17}O NMR signal with a shoulder on the high-field side for the uranyl oxygens in 6 M (1 M = 1 mol dm^{-3}) perchloric acid solution, and two peaks in 0.2 M perchloric acid solution. Rabideau suggested that these results may be due to the formation of polynuclear species of uranyl ions. However, the formation of polynuclear species is unlikely in highly acidic solutions.[2,3] He did not take account the difference in ^{17}O enrichment in the uranyl oxygens.

In order to examine Rabideau's results, we have observed the ^{17}O NMR spectra of the uranyl ion in solutions with different acid concentrations, and the effect of ^{17}O enrichment in the uranyl oxygens on the ^{17}O NMR spectrum.

Experimental

Uranyl perchlorate pentahydrate was prepared by dissolving $UO_3 \cdot 2H_2O$ in 60% perchloric acid (Wako Pure Chemical Ind. Ltd.). The $UO_3 \cdot 2H_2O$ was prepared by using the method of Ekstrom *et al.*[4] The uranyl perchlorate pentahydrate was recrystallized from distilled water five times, and the resulting crystals were dried *in vacuo*. The abundance of ^{17}O in enriched water used was 20.5 atom % (Merck, ^{16}O: 50.4, ^{18}O: 29.1 atom %) and 42.1 atom % (Merck, ^{16}O: 26.3, ^{18}O: 31.7 atom %). Uranyl oxygens were enriched by irradiation of uranyl perchlorate solution containing ^{17}O-enriched water with a 500-W high pressure mercury lamp.[5] Samples for the NMR measurements were prepared by adding D_2O (Merck) and perchloric acid to the enriched uranyl perchlorate solution, followed by introducing the sample solution into the NMR microcell (Wilmad). The microcell was inserted in 10 mm o.d. NMR tube (Wilmad) containing reference water. Measurements of the ^{17}O NMR spectra were carried out at 13.46 MHz on a JEOL JNM-FX 100 FT-NMR spectrometer. Typical spectral settings for the measurements of ^{17}O NMR spectra are as follows: 4K data points, 90° pulse angle corresponding to *ca.* 10 μs pulse width, 500 Hz spectral width, 1.95 ms recycle delay, and normally 5000 scans. Temperature was maintained at 293±1 K.

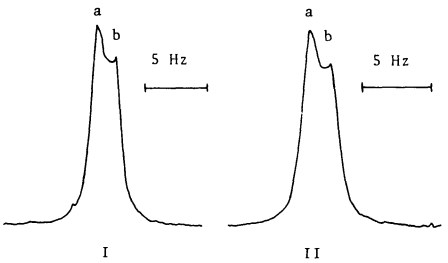

Fig. 1. ^{17}O NMR spectra of the uranyl oxygens at different acid concentrations. The uranyl oxygens were enriched by using $H_2{}^{17}O$ (20.5 atom %).
I: $[UO_2^{2+}]=0.078$ m, $[H^+]=0.22$ m, II: $[UO_2^{2+}]=0.12$ m, $[H^+]=6.0$ m.

Results and Discussion

The ^{17}O NMR spectra of the uranyl oxygens which were enriched by using $H_2{}^{17}O$ (20.5 atom %) were measured at different acid concentrations. The ^{17}O signal of uranyl oxygens was observed at *ca.* +1119 ppm[6] relative to water in 0.22 and 60 m (1 m=1 mol kg^{-1}) perchloric acid solutions. This result is in good agreement with those of earlier works.[1,7] Figure 1 shows the expanded ^{17}O signals of the uranyl oxygens, where no difference was observed in the lineshapes. The difference in chemical shifts between two peaks a and b was determined to be 0.107 ± 0.002 ppm.

The ^{17}O signal of the uranyl oxygens which were enriched by using $H_2{}^{17}O$ (42.1 atom %) was also measured in a 0.23 m perchloric acid solution, and the result is shown in Fig. 2. It is noted that the ^{17}O signal has three peaks p, q, and r, and peaks q and r are observed at -0.054 ± 0.002 and -0.108 ± 0.002 ppm from peak p, respectively. The difference in chemical shifts between two peaks a and b shown in Fig. 1 is the same as that between two peaks p and r shown in Fig. 2 within experimental errors. This result indicates that peak b corresponds to peak r.

From the results in Figs. 1 and 2, it is clear that the ^{17}O NMR lineshape of the uranyl oxygens does not depend on the acid concentration, but depends on the ^{17}O enrichment in the uranyl oxygens. This fact suggests that the change of lineshape is due to the difference in ratio of relative concentration of isotopomers of the uranyl ion, because the ratio changes with the ^{17}O enrichment in the uranyl oxygens.

As the uranyl ion has three isotopomers which are active for ^{17}O NMR, *i.e.*, $[^{16}O=U=^{17}O]^{2+}$, $[^{17}O=U=^{17}O]^{2+}$, and $[^{18}O=U=^{17}O]^{2+}$, three peaks in Fig. 2 may be assigned to these isotopomers. This deduction is supported

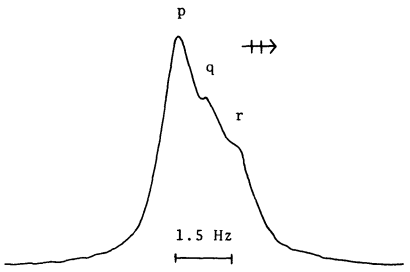

Fig. 2. ^{17}O NMR spectrum of the uranyl oxygens enriched by using $H_2{}^{17}O$ (42.1 atom %). $[UO_2^{2+}]=0.098$ m and $[H^+]=0.23$ m.
Conditions of enrichment: each weight of $UO_2(ClO_4)_2 \cdot 5H_2O$ and $H_2{}^{17}O$ was 1.023 g and 0.3978 g, respectively.

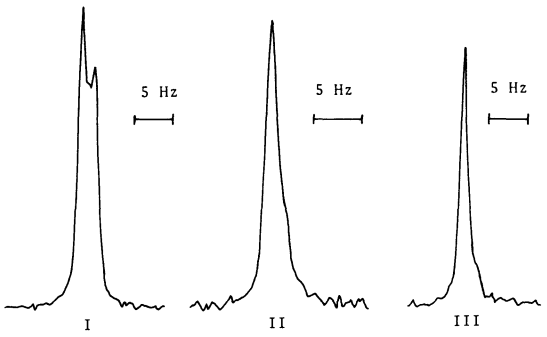

Fig. 3. Change in ^{17}O signals of the enriched uranyl oxygens by irradiation. The uranyl oxygens were enriched by using $H_2{}^{17}O$ (20.5 atom %). $[UO_2^{2+}]$= 0.065 m and $[H^+]$=3.8 m.
I: Before irradiation, II: after irradiation for 10 min, III: after irradiation for 15 min.

by the following results. Figure 3 shows the spectral change of ^{17}O signal of the uranyl oxygens by the irradiation of the enriched uranyl perchlorate solution with the mercury lamp. As is seen in Fig. 3, the intensity of the peak at high-field side decreases gradually with increasing the irradiation time. This phenomenon must be caused by oxygen exchange between the uranyl ion and bulk water, resulting in the variation of relative concentration ratio of three isotopomers. Hence, the peak at the lowest field in Fig. 3, which corresponds to peak a or p in Figs. 1 or 2, respectively, can be assigned to the signal of $[^{16}O{=}U{=}^{17}O]^{2+}$ isotopomer. The concentration of $[^{16}O{=}U{=}^{17}O]^{2+}$ is estimated to be at least ten times those of $[^{17}O{=}U{=}^{17}O]^{2+}$ and $[^{18}O{=}U{=}^{17}O]^{2+}$ at the exchange equilibrium after irradiation. Moreover, in view of the usual trend in the isotope effect on chemical shifts that the magnitude of the upfield shift is largest where the fractional change in mass upon substitution is largest,[8] peaks q and r in Fig. 2 may be assigned to the signals of $[^{17}O{=}U{=}^{17}O]^{2+}$ and $[^{18}O{=}U{=}^{17}O]^{2+}$, respectivery. As a result, peak b in Fig. 1 may be assigned to the signal of $[^{18}O{=}U{=}^{17}O]^{2+}$, since peak b corresponds to peak r as mentioned above. Although the ^{17}O signal of $[^{17}O{=}U{=}^{17}O]^{2+}$ was not able to be observed in Fig. 1, this result may arise from the fact that the relative concentration of $[^{17}O{=}U{=}^{17}O]^{2+}$ is low compared with those of $[^{16}O{=}U{=}^{17}O]^{2+}$ and $[^{18}O{=}U{=}^{17}O]^{2+}$.

From the conditions given in Fig. 2, we can calculate the probability for the occurrence of three isotopomers, assuming that oxygen isotopes are distributed statistically without the isotope effect in O=U=O bond. The ratio of probabilities is given as follows: $P_{16,17}$: $P_{17,17}$: $P_{18,17}$[9]=0.282: 0.0676: 0.102. Therefore, the ratio of relative intensities of three isotopomers is estimated as follows: $I_{16,17}$: $I_{17,17}$: $I_{18,17}$[9]=2.76: 1.32: 1.00. Assuming that the whole lineshape in Fig. 2 is formed by overlapping of three Lorentzian curves with the same linewidth, the best-fit calculated lineshape gives the ratio of relative intensities of three peaks p, q, and r as follows: I_p: I_q: I_r= 2.50: 1.00: 1.07. This ratio is in fair agreement with the calculated ratio of $I_{X,Y}$ from $P_{X,Y}$ values under the conditions given in Fig. 2.

It appears well established that the ^{17}O NMR spectra of uranyl oxygens have three peaks corresponding to three isotopomers of the uranyl ion, where the peak at the lowest field is assigned to the signal of $[^{16}O{=}U{=}^{17}O]^{2+}$ and the signals of $[^{17}O{=}U{=}^{17}O]^{2+}$ and $[^{18}O{=}U{=}^{17}O]^{2+}$ shift to the higher field by 0.054±0.002 and 0.108±0.002 ppm relative to $[^{16}O{=}U{=}^{17}O]^{2+}$. This result is the first finding with respect to the isotope shift through two equivalent bonds in ^{17}O NMR.

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References

1) S. W. Rabideau, *J. Phys. Chem.*, **71**, 2747 (1967).
2) C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962).
3) R. M. Rush and J. S. Johnson, *J. Phys. Chem.*, **67**, 821 (1963).
4) A. Ekstrom, H. Loeh, C. H. Randall, L. Szego, and J. C. Taylor, *Inorg. Nucl. Chem. Lett.*, **14**, 301 (1978).
5) G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **16**, 272 (1961); K. Okuyama, Y. Ishikawa, Y. Kato, and H. Fukutomi, *Bull. Res. Lab. Nucl. Reactor*, **3**, 39 (1978).
6) IUPAC recommendations. *Pure Appl. Chem.*, **45**, 219 (1976).
7) L. G. Mashirov, D. V. Suglobov, and V. A. Scherbakov, *Radiokhimiya*, **17**, 881 (1975).
8) H. Batiz-Hernandez and R. A. Bernheim, *Prog. Nucl. Magn. Reson. Spectrosc.*, **3**, 63 (1967).
9) $P_{X,Y}$ and $I_{X,Y}$ refer to the probability for the occurrence and the relative intensity of $[^{x}O{=}U{=}^{y}O]^{2+}$ isotopomer, respectively.