December, 1986] Bull. Chem. Soc. Jpn., 59, 3761—3764 (1986) 3761

Oxygen-17 NMR Study of the Uranyl Ion. III.[1] Factors Influencing ^{17}O Chemical Shifts of Uranyl Oxygens in Aqueous Perchlorate Media

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(Received May 29, 1986)

Effects of concentrations of perchlorate ion, nitrate ion, uranyl ion, and acid, isotopic substitutions, and temperature on ^{17}O chemical shifts of oxygen in the uranyl ion (uranyl oxygens hereafter) have been studied in aqueous perchlorate media. Insensitivity of the ^{17}O chemical shifts to $[ClO_4^-]$ leads to the conclusion that the perchlorate ion is not coordinated to the uranyl ion. The stability constant (0.10 ± 0.04 m^{-1} at 25 °C and ionic strength 5.0 m; m=mol kg^{-1}) of a $UO_2NO_3^+$ complex has been obtained from the dependence of the ^{17}O chemical shifts on $[NO_3^-]$. The ^{17}O resonances shift toward the lower field with increasing concentrations of uranyl ion and acid, indicating the possibilities of the dimer formation of the uranyl ion and the protonation of uranyl oxygen atoms in concentrated solution, respectively. Isotope shifts in ^{17}O nuclear magnetic shielding in the uranyl ion are interpreted in terms of the change of mean separation between the ground and lowest excited electronic states upon oxygen and uranium isotopic substitutions. Temperature dependence of ^{17}O chemical shifts is discussed in connection with the isotope effects.

The aqueous solution chemistry of a uranyl ion (UO_2^{2+}) is fundamental and important in understanding chemical and physical properties of the uranyl ion. In spite of many studies on the aqueous solution chemistry, there remain several unsolved problems in the uranyl ion in aqueous solution, e.g. whether or not a counter ion (perchlorate or nitrate ion) is coordinated to the uranyl ion, or whether uranyl oxygen atoms are chemically inert. ^{17}O chemical shifts of uranyl oxygens were reported to be sensitive to the base strength of ligands in the equatorial plane.[1] The ^{17}O chemical shifts were correlated with the reciprocal of the lowest electronic transition energies of uranyl complexes in nonaqueous solvents. ^{17}O NMR spectroscopy plays an important role in studying the uranyl ion because of the sensitivity of ^{17}O chemical shifts to chemical surroundings and the electronic structure of the uranyl ion. In order to pursue the above-mentioned problems in aqueous solution chemistry of the uranyl ion, we have investigated effects of concentrations of perchlorate ion, nitrate ion, uranyl ion, and acid on ^{17}O chemical shifts of uranyl oxygens in aqueous perchlorate solution.

The oxygen isotope effect on ^{17}O NMR spectra of uranyl oxygens reported in previous papers[1,2] will be interpreted on the basis of spectroscopic information which is currently available for the uranyl ion. Temperature dependence of ^{17}O chemical shifts of uranyl oxygens is measured and discussed in connection with the isotope effects in ^{17}O chemical shifts.

Experimental

The uranyl complex and acid used were uranyl perchlorate pentahydrate $UO_2(ClO_4)_2\cdot5H_2O$[2] and 60% perchloric acid (Wako Pure Chemical Ind., Ltd.), respectively. Sodium perchlorate(Wako) and sodium nitrate (Wako) were recrystallized twice from aqueous solution before use. The ionic strength was adjusted by using sodium perchlorate. Procedure for preparation of ^{17}O-enriched uranyl oxygens is described in the previous paper.[2] A 5 mm o.d. NMR sample tube was immersed in a 10 mm o.d. NMR tube containing $(CD_3)_2CO$ (Merck). Measurements of ^{17}O NMR spectra were carried out at 13.46 MHz on a JEOL JNM-FX 100 FT-NMR spectrometer equipped with a JNM-VT-3B temperature controller. Typical spectral settings for the measurements of ^{17}O NMR spectra are as follows: 8 K data points, 90° pulse angle corresponding to ca. 10 μs pulse width, 10 or 20 kHz spectral width (leading to 2.44 or 4.88 Hz digital resolution), and normally 2000 scans.

Results and Discussion

Effects of Concentrations of Perchlorate Ion, Nitrate Ion, Uranyl Ion, and Acid. Addition of $NaClO_4$ (up to 1.5 m) to the solution, where $[UO_2^{2+}]=0.02$ m and $[H^+]=0.06$ m, did not change ^{17}O chemical shifts of uranyl oxygens, while ^{17}O resonance of solvent H_2O shifted toward the higher field by the addition.[3] The former result indicates that the perchlorate ion is not coordinated to the uranyl ion in solution[4,5] as in the solid state.[6] In contrast to the result on the effect of the perchlorate ion, the addition of $NaNO_3$ to the solution, where $[UO_2^{2+}]=0.11$ m and $[H^+]=0.08$ m at ionic strength 5.0 m, increased ^{17}O chemical shifts of uranyl oxygens relative to $(CD_3)_2CO$ at 25 °C, as shown in Fig. 1. This result can be explained by the formation of a $UO_2NO_3^+$ complex:

$$UO_2^{2+} + NO_3^- \overset{K_1}{\rightleftharpoons} UO_2NO_3^+ \qquad (1)$$

Assuming that $[NO_3^-]\gg[UO_2^{2+}]$ and the equilibrium reaction is very fast, the observed ^{17}O chemical shifts $\delta(^{17}O)_{obsd}$ is given by

$$\delta(^{17}O)_{obsd} = \delta(^{17}O) + \frac{\Delta\delta K_1[NO_3^-]}{1+K_1[NO_3^-]} \qquad (2)$$

or

$$\frac{1}{\delta(^{17}O)_{obsd}-\delta(^{17}O)} = \frac{1}{\Delta\delta}\left(1+\frac{1}{K_1[NO_3^-]}\right), \qquad (3)$$

where $\delta(^{17}O)$ is the ^{17}O chemical shift of the UO_2^{2+} ion and $\Delta\delta$ is the difference in ^{17}O chemical shift between UO_2^{2+} and $UO_2NO_3^+$ ions. The positive value of $\Delta\delta$ is

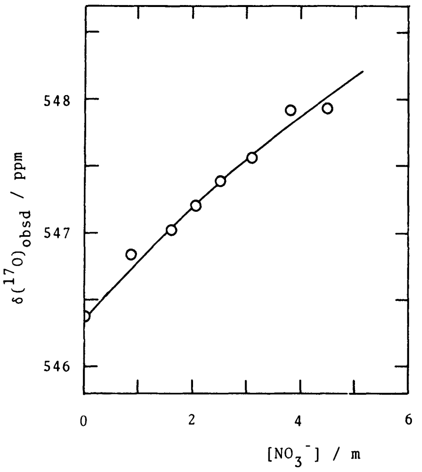


Fig. 1. Dependence of ^{17}O chemical shifts of uranyl oxygens on $[NO_3^-]$ at 25°C and ionic strength 5.0 m. $[UO_2^{2+}]=0.11$ m and $[H^+]=0.08$ m. The ^{17}O chemical shift is referred to external $(CD_3)_2CO$.

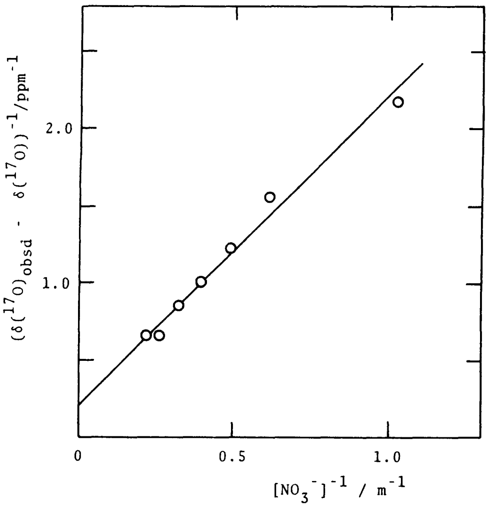


Fig. 2. A plot of $1/(\delta(^{17}O)_{obsd}-\delta(^{17}O))$ vs. $1/[NO_3^-]$ at 25°C and ionic strength 5.0 m. $[UO_2^{2+}]=0.11$ m and $[H^+]=0.08$ m.

expected from the bathochromic shift of electronic absorption bands by the complexation of NO_3^- ion.[1,7] Figure 2 shows a linear relationship between $1/(\delta(^{17}O)_{obsd}-\delta(^{17}O))$ and $[NO_3^-]^{-1}$, as expected from Eq. 3. The formation constant K_1 of $(0.10\pm0.04)\ m^{-1}$ was calculated from the slope and intercept in Fig. 2. This value is comparable to the literature values: $0.15\ M^{-1}$ ($M=mol\ dm^{-3}$) at ionic strength 6.25 M[4] and $0.21\ M^{-1}$ at ionic strength 5.38 M.[8] The value of $\Delta\delta$ was determined to be (4.9 ± 2.1) ppm at 25 °C.

The $\delta(^{17}O)$ values relative to $(CD_3)_2CO$ at 25 °C increased linearly with increasing concentration of the uranyl ion up to 1.5 m in acidic solution ($[H^+]=0.06$ m), i.e. $d\delta(^{17}O)/d[UO_2^{2+}]=(0.57\pm0.11)\ ppm\ m^{-1}$. This may suggest the possibility of the dimer formation of the uranyl ion

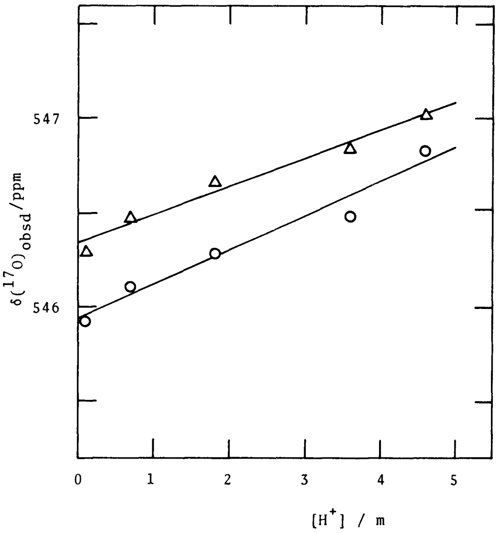
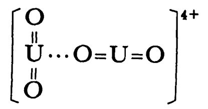


Fig. 3. Dependence of ^{17}O chemical shifts of uranyl oxygens on the acid concentration at 25(○) and 39(△)°C. $[UO_2^{2+}]=0.1$ m and ionic strength=5.0 m. The ^{17}O chemical shift is referred to external $(CD_3)_2CO$.



$$\left[\begin{array}{l} O \\ \| \\ U\cdots O{=}U{=}O \\ \| \\ O \end{array}\right]^{4+}$$

with increasing concentration of the uranyl ion. The coordination ability of uranyl oxygen atoms is well known for $UO_2(\beta\text{-diketonate})_2$ complexes.[9] The fact that the hydration number of the uranyl ion decreases with lowering H_2O/UO_2^{2+} mole ratios may not be due to the inner-sphere coordination of ClO_4^- as indicated by Åberg et al.,[5] but be due to the dimer formation.

Figure 3 shows that ^{17}O chemical shifts of uranyl oxygens increase with increasing acid concentration. This can be explained by the following fast equilibrium reaction.[10,11]

$$UO_2^{2+} + H^+ \overset{K_2}{\rightleftharpoons} UO_2H^{3+} \qquad (4)$$

Assuming that $K_2[H^+]\ll1$, the observed ^{17}O chemical shift $\delta(^{17}O)_{obsd}$ is given by $\delta(^{17}O)+\{\delta'(^{17}O)-\delta(^{17}O)\}K_2[H^+]$, where $\delta'(^{17}O)$ and $\delta(^{17}O)$ are ^{17}O chemical shifts of uranyl oxygens in the protonated and unprotonated uranyl ion, respectively. Thus the slopes in Fig. 3 correspond to $\{\delta'(^{17}O)-\delta(^{17}O)\}K_2$, whose values are determined to be (0.18 ± 0.02) and (0.15 ± 0.02) $ppm\ m^{-1}$ at 25 and 39 °C, respectively.

Isotope Shifts. We reported in the previous paper[1] that chemical shifts for the signals of $[^{17}O{=}U{=}^{17}O]^{2+}$ and $[^{18}O{=}U{=}^{17}O]^{2+}$ isotopomers were observed to be -0.059 and -0.117 ppm, respectively, relative to $[^{16}O{=}U{=}^{17}O]^{2+}$. To our knowledge, these isotope shifts are the first finding with respect to two-bond isotope shifts in ^{17}O NMR spectroscopy, and we have attempted to elucidate the origin of these shifts.

The nuclear magnetic shielding is the sum of diamagnetic (σ_d) and paramagnetic (σ_p) terms. The latter

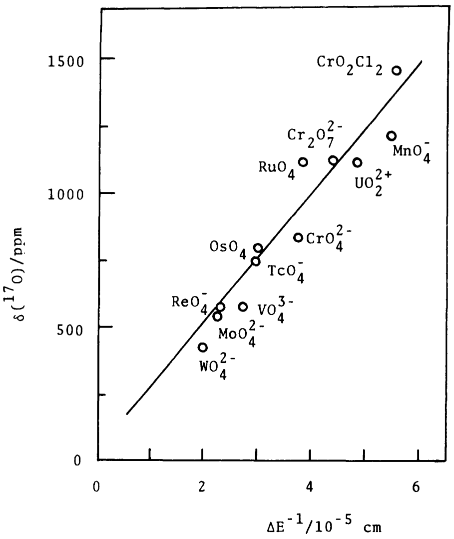


Fig. 4. A plot of ^{17}O chemical shifts vs. the reciprocal of the lowest electronic transition energies for compounds containing oxygen bonded to transition metals. ^{17}O chemical shifts are reported downfield from external water.

Table 1. Vibrational Frequencies (cm^{-1}) of Isotopomers of the $^{238}UO_2{}^{2+}$ Ion in Aqueous Solution

Isotopomer	ω_{01}	ω_{02}	ω_{03}
$[^{16}O{=}U{=}^{16}O]^{2+}$	881[a]	210[b]	963[c]
$[^{16}O{=}U{=}^{17}O]^{2+}$	868	207	950
$[^{17}O{=}U{=}^{17}O]^{2+}$	855	204	938
$[^{18}O{=}U{=}^{17}O]^{2+}$	843	202	926

a) Y. Tanaka, Y. Fujii, and M. Okamoto, *J. Phys. Chem.*, **86**, 1015 (1982). b) F. A. Hart and J. E. Newbery, *J. Inorg. Nucl. Chem.*, **30**, 318 (1968). c) Ref. 17

Table 2. Isotope Shifts in ^{17}O Nuclear Magnetic Shielding

Compound	Isotope shift/ppm	Ref.
$[^{17,18/16}O{=}U{=}^{17}O]^{2+}$	0.059, 0.117	1
$[^{16}O{=}^{235/238}U{=}^{17}O]^{2+}$	-2×10^{-3}	This work
$^{101/99}Ru^{16}O_3{}^{17}O$	0.02	23
$^{13/12}C^{17}O$	0.110	24
$^{16}O{=}^{13/12}C{=}^{17}O$	0.143	24
$D_2{}^{17}O/H_2{}^{17}O$[a]	3.08	25

a) In liquid phase.

term is proportional to the reciprocal of the mean transition energy (ΔE) between the ground and excited electronic states,[12] which is obtained by averaging over the vibrational levels of these states. Benedek et al.[13] investigated the dependence of ΔE upon the vibrational frequencies, ω_0 and ω_1, in the ground and excited states. In the temperature range studied ($\omega_{0j} > kT$), the vibronic dependence of the nuclear magnetic shielding for a single excited state can be expressed by

$$\sigma = \sigma_d + \sigma_p\left\{1 + \sum_{j=1}^{p}(4\Delta E_0)^{-1}\left[1-\left(\frac{\omega_{1j}}{\omega_{0j}}\right)^2\right]\omega_{0j}\right\}, \qquad (5)$$

where ΔE_0 is the separation of the ground and excited electronic states at the zero vibrational levels, and the summation is carried out over the p normal vibration mode. Since the ratio ω_{1j}/ω_{0j} will not be affected by isotopic substitution, the two-bond oxygen-isotope shift ($\Delta\sigma_{x,y}$)[14] in ^{17}O nuclear shielding of uranyl oxygens (($^2\Delta^{17}O(^{17,18/16}O)$)[15] is given by

$$\begin{aligned}\Delta\sigma_{x,y} &= \sigma_{x,y} - \sigma_{16,17}\\ &= \frac{B}{4(\Delta E)^2}\sum_{j=1}^{p}\left[1-\left(\frac{\omega_{1j}}{\omega_{0j}}\right)^2\right](\omega_{0j}^{x,y}-\omega_{0j}^{16,17}).\end{aligned} \qquad (6)$$

Parameter B (-2.50×10^7ppm cm) can be obtained from the slope in Fig. 4, which shows a linear relationship between the ^{17}O chemical shifts and the reciprocal of the lowest electronic transition energies for compound containing oxygen bonded to transition metals.[16] The ω_{1j}/ω_{0j} value can be taken as $(f_1/f_0)^{1/2}$, where f_0 (7.52 mdyne Å^{-1})[17] and f_1 (6.54 mdyne Å^{-1})[18] are force constants in the ground and lowest excited states, respectively. If three vibrations in the UO_2 unity are assumed to be harmonic and the force constants are unchanged by isotopic substitutions, the effect of isotopic substitutions on vibrational frequencies can be calculated theoretically.[19] The calculated vibrational frequencies in the ground states for various isotopomers are listed in Table 1. The values for a $[^{16}O{=}U{=}^{16}O]^{2+}$ isotopomer are those obtained experimentally for the uranyl ion in aqueous solution. The calculated $\Delta\sigma_{17,17}$ and $\Delta\sigma_{18,17}$ from Eq. 6 are 0.063 and 0.12 ppm, respectively, which agree surprisingly with the experimental results, when considered the assumptions involved in deriving Eq. 6 and estimating the parameters. The calculated difference (1.9 cm^{-1}) in the lowest electronic transition energies between $[^{16}O{=}U{=}^{17}O]^{2+}$ and $[^{18}O{=}U{=}^{17}O]^{2+}$ isotopomers for the hydrated uranyl ion is of the same order as that (5.0 cm^{-1}) obtained experimentally for $Cs_2UO_2Cl_4$.[20]

The one-bond uranium isotope shift in ^{17}O nuclear shielding ($^1\Delta^{17}O(^{235/238}U)$),[15] which is defined by $\sigma([^{16}O{=}^{235}U{=}^{17}O]^{2+})-\sigma([^{16}O{=}^{238}U{=}^{17}O]^{2+})$, can be estimated in a similar way. The estimated isotope shift of -2×10^{-3} ppm is too small compared with the linewidth (ca. 1 Hz) of ^{17}O resonance of uranyl oxygens. This might make it difficult to observe the uranium isotope effect in the ^{17}O NMR spectrum. It is noted that no uranium isotope effect was observed in ^{19}F nuclear shielding for UF_6.[21] Isotope shifts in ^{17}O nuclear shieldings so far reported are summarized in Table 2, which shows that the isotope shift becomes larger with increasing fractional change in mass upon isotopic substitution.[22]

Temperature Dependence. We investigated the temperature dependence of ^{17}O chemical shift of uranyl oxygens and the results are shown in Fig. 5. The ^{17}O resonances of the uranyl oxygens shift toward the lower field with increasing temperature ((0.087±0.002) ppm °C^{-1}), whereas the ^{17}O resonances of solvent H_2O

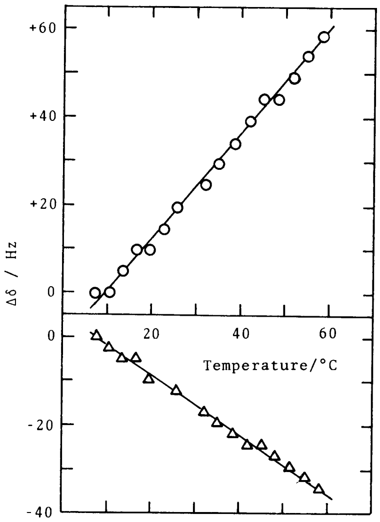


Fig. 5. Temperature dependence of ^{17}O resonances of uranyl oxygens (O) and solvent H_2O (Δ). The positive sign means the shift to the lower field. $[UO_2^{2+}]=0.32$ M and $[H^+]=0.01$ M.

shift toward the higher field with temperature ((-0.050 ± 0.001) ppm °C^{-1}). The latter is due to the increasing fraction of broken hydrogen bonds with temperature.[3] The former result is in accord with that for temperature dependence of magnetic susceptibility, i.e. the uranyl ion becomes more paramagnetic as the temperature increases.[26] Bell and Biggers[27] resolved the overlapping bands in the absorption spectrum of the uranyl ion in aqueous solution and studied the temperature dependence of position of each band. They showed that the positions of all the bands shift linearly toward the red with increasing temperature. This result consists with that for the temperature dependence of ^{17}O chemical shifts in view of the fact that ^{17}O chemical shifts of uranyl oxygens for uranyl complexes in nonaqueous solvents increase as absorption bands of the complexes shift toward the red.[1]

Changes in ^{17}O nuclear shielding of uranyl oxygens with temperature can arise from the following effects: (1) variation of effective separation between the ground and excited states because of thermal statistical occupancy of the ground vibrational levels[13]; (2) thermal expansion of U=O bond length with increasing temperature, where the energy separation between the ground and excited states is calculated to increase with decreasing U=O bond length.[28]

Effects of temperature and isotopic substitutions on ^{17}O nuclear shielding of uranyl oxygens may be also explained by using Jameson's model,[29] where the nuclear shielding is considered as an electronic property which depends on the relative positions of nuclei. The heavier isotopomer has smaller amplitude of motion than a lighter one on the same potential surface, while the average amplitude of vibrational motion increases with temperature. Thus the average U=O bond length is expected to vary with isotopic substitution and temperatue, resulting in the change in ^{17}O nuclear shielding.

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