

Oxidation of Uranium(IV) by Nitrite Ion in Dimethyl Sulfoxide.
Evidence of Direct Oxygen Transfer Mechanism

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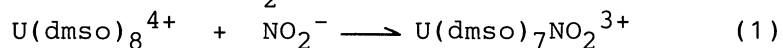
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The oxidation of $[\text{U}(\text{dmsO})_8]^{4+}$ (dmsO = dimethyl sulfoxide) by nitrite ion was studied in dmsO. The reaction was found to proceed via two steps: the first step was the rapid formation of 1 : 2 complex between U(IV) and nitrite ion, and the second one the intra-molecular oxygen transfer reaction from nitrite to U(IV). The latter step was confirmed by oxygen labeled experiments using ^{17}O -NMR.

In the nuclear fuel reprocessing, reactions of nitrous acid or nitrite ion with uranium and transuranium ions are of particular importance. However, little is known with respect to the reaction mechanisms because of the complex behavior of HNO_2 (or NO_2^-) acting as an oxidant or reductant.¹⁾ In this paper, we report the study on the oxidation of $[\text{U}(\text{dmsO})_8]^{4+}$ by nitrite ion in dmsO and propose a detailed reaction mechanism.

The UV-visible absorption spectra of $[\text{U}(\text{dmsO})_8(\text{ClO}_4)_4]$ in dmsO containing various concentrations of NaNO_2 was measured by using a Shimadzu UV-365 spectrophotometer. $[\text{U}(\text{dmsO})_8(\text{ClO}_4)_4]$ was prepared by the reported method²⁾ and verified from the absorption spectrum. Figure 1 shows the spectroscopic titration of $[\text{U}(\text{dmsO})_8(\text{ClO}_4)_4]$ by the addition of NaNO_2 in dmsO. No appreciable gain in absorbance characteristic of U(VI) was observed in the wavelength region below 430 nm. This observation indicates that U(IV) is not oxidized by nitrite under conditions with $[\text{NaNO}_2] < [\text{U(IV)}]$. The change in the spectra in Fig. 1 with eight isosbestic points could be explained by the formation of a 1 : 1 complex between U(IV) and NO_2^- as follows:



On the other hand, U(IV) began to be oxidized to U(VI), if the initial

concentration of nitrite was larger than that of U(IV). Figure 2 shows the spectral change with time under the stoichiometric condition $[\text{NaNO}_2] = 2[\text{U(IV)}]$. The decrease in absorbance at 660 nm and the simultaneous increase at 430 nm with time shows the oxidation of U(IV) to U(VI). However, when the solution was acidified by adding perchloric acid, no appreciable change was observed in the absorption spectrum for several hours. This clearly indicates that only NO_2^- instead of HNO_2 oxidizes U(IV).

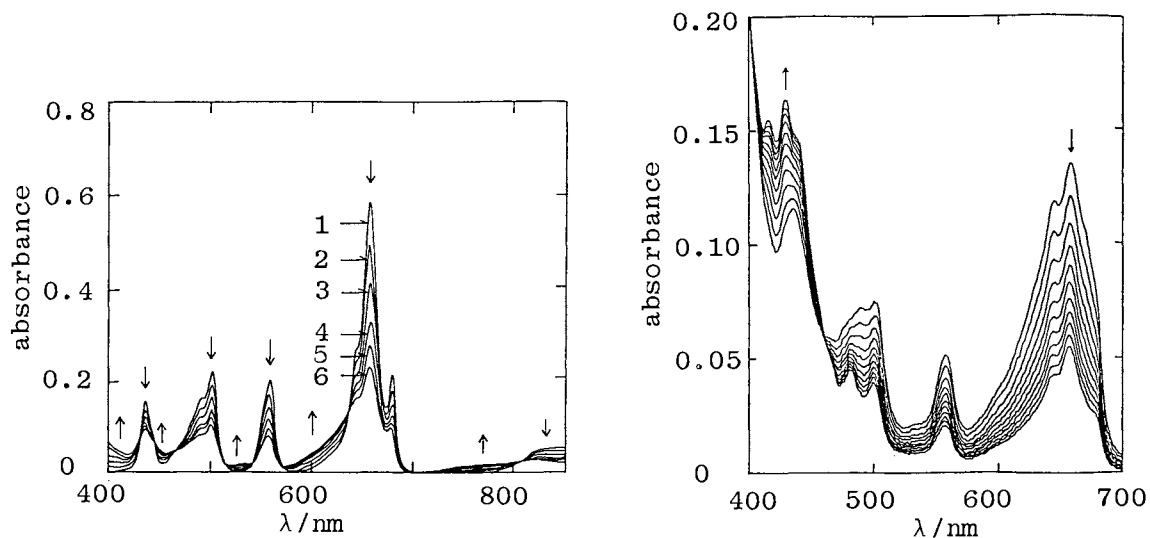


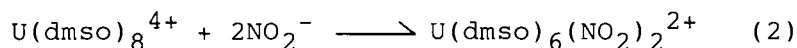
Fig. 1. Change in UV-visible absorption spectra of $\text{U(dmso)}_8(\text{ClO}_4)_4$ in dmso by the addition of various concentrations of NaNO_2 at 20 °C.

$[\text{U(dmso)}_8(\text{ClO}_4)_4] = 0.005 \text{ mol dm}^{-3}$ and $[\text{NaNO}_2] = 0$ (1), 0.001 (2), 0.002 (3), 0.003 (4), 0.004 (5), and 0.005 mol dm^{-3} (6).

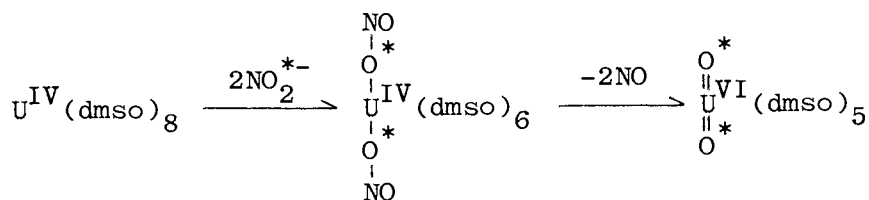
Fig. 2. UV-visible absorption spectra of the dmso solution containing $\text{U(dmso)}_8(\text{ClO}_4)_4$ and twice molar equivalent NaNO_2 as a function of time. Measurements were made at 2 minutes intervals under the initial conditions $[\text{U(dmso)}_8(\text{ClO}_4)_4] = 0.005 \text{ mol dm}^{-3}$ and $[\text{NaNO}_2] = 0.010 \text{ mol dm}^{-3}$ at 20 °C.

The short time scale interaction between $\text{U(dmso)}_8(\text{ClO}_4)_4$ and NO_2^- was examined by using a Union Giken RA-401 stopped-flow spectrophotometer. The rate was extremely fast being over within 20 ms at 20 °C. Therefore, transient spectra were measured at 20 ms after the mixing. Figure 3 shows the transient spectra for two cases: A) $[\text{U(IV)}] : [\text{NaNO}_2] = 1 : 1$; B) $[\text{U(IV)}] : [\text{NaNO}_2] = 1 : 2$. There exists considerable difference in the spectra A and B. Since the spectrum A agrees with the normal absorption spectrum measured under the same condition, the 1 : 1 complex between U(IV) and nitrite should be formed rapidly. It appears likely that the 1 : 2 complex is also formed similarly under the condition $[\text{NaNO}_2] = 2[\text{U(IV)}]$,

giving the spectrum B. The reaction can be written below:



If an oxygen atom (or more likely O^-) transfers from NO_2^- to $\text{U}(\text{IV})$ in this complex by the following scheme, $\text{U}(\text{IV})$ should be oxidized to $\text{U}(\text{VI})$ as a result.



In order to confirm this scheme, ^{17}O -NMR measurements were carried out by using a JEOL JNM FX-100 NMR spectrometer. ^{17}O enriched NaNO_2 was prepared by bubbling NO gas into sodium hydroxide aqueous solution, which was made by dissolving NaOH in 10% ^{17}O enriched water. In this method, nearly 4% ^{17}O enriched NaNO_2 can be prepared. $\text{U}(\text{dmsO})_8(\text{ClO}_4)_4$ (0.01 mol dm^{-3}) was mixed with excess amount of NaNO_2 (about twenty times) in dmsO-d_6 and the ^{17}O -NMR spectrum was recorded after the completion of reaction. In Fig. 4, a narrow peak at 1131.5 ppm down field from water

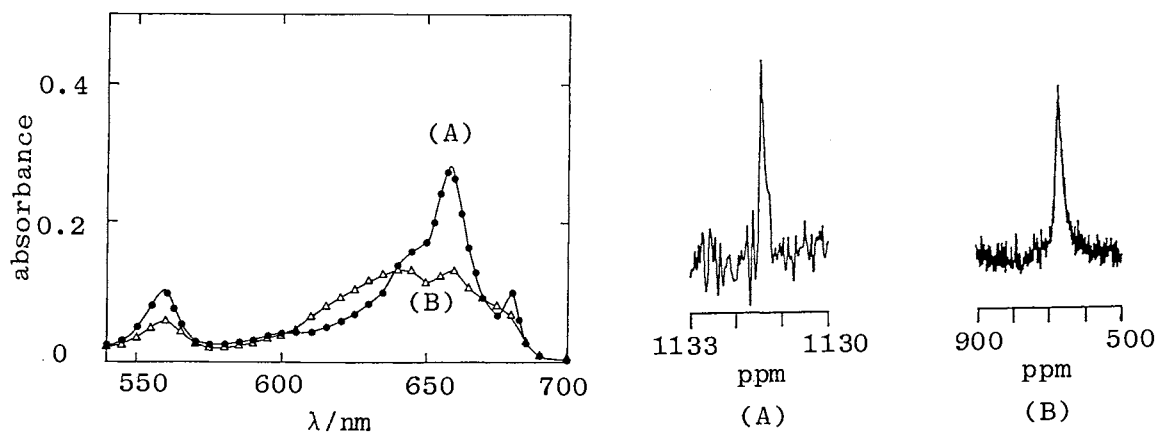


Fig. 3. Transient absorption spectra (20 ms after mixing) for the reaction of $\text{U}(\text{dmsO})_8(\text{ClO}_4)_4$ and NaNO_2 in dmsO at 20°C . The spectra A and B correspond to the following initial conditions: A, $[\text{U}(\text{IV})] : [\text{NaNO}_2] = 1 : 1$ (●); B, $[\text{U}(\text{IV})] : [\text{NaNO}_2] = 1 : 2$ (Δ).

Fig. 4. ^{17}O -NMR spectra of $\text{UO}_2(\text{dmsO})_5^{2+}$ (A) and NaNO_2 (B) in dmsO-d_6 .

signal can be assigned to that of $\text{UO}_2(\text{dmsO})_5^{2+}$ in comparison with the earlier results,³⁾ i.e. the chemical shift of $\text{UO}_2(\text{dmsO})_5^{2+}$ was reported to be 1129.7 ppm from water and such a narrow ^{17}O -NMR spectrum was known only in uranyl oxygens. A broad peak at 670 ppm from water was consistent with the reported value for the signal of nitrite ion.⁴⁾ The same experiment was made using normal water, but no ^{17}O -NMR signal was observed. These findings clearly indicate that oxygen atoms transfer from nitrite to U(IV) passing through the above reaction scheme, resulting in the oxidation of U(IV) to U(VI).

The mechanism of oxidations of U(IV) to U(VI) has been discussed for long years. Consecutive one electron transfer reactions through U(V) were reported for the oxidation of U(IV) by Fe(III) ion in aqueous solution.⁵⁾ On the other hand, Gordon and Taube showed a direct oxygen atom transfer mechanism for the oxidation of aqueous U(IV) with oxygen-containing oxidizing agents, PbO_2 and MnO_2 .⁶⁾ The present study also shows the direct conversion from U(IV) to U(VI) through the oxygen transfer mechanism. A detailed kinetic study for the reaction between U(IV) and nitrite is in progress.

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