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Anion-dependent electron paramagnetic resonance of uranium(V) intermediates in photo- and electrolytic reductions of uranyl complexes in organic solution

C. Miyake and Y. Sano
Faculty of Engineering, Osaka University, Suita, Osaka 565 (Japan)

Abstract

Electron paramagnetic resonance (EPR) and optical spectra of uranium(V) were observed in both photo- and electrolytic reductions of uranyl-TIBP (triisobutylphosphate) and uranyl-CMPO (octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide) complexes with the counter-ions NO_3^- and ClO_4^- in several organic solutions. In addition, IR spectra and cyclic voltammograms were measured. The EPR signals of all these complexes during the electrolytic reduction and of the uranylperchlorate complexes during the photoreduction are broad and the values of the *g* factor are larger than 2.0. On the other hand, sharp signals were recorded for the uranylnitrate complexes during the photoreduction and the values of the *g* factor are smaller than 2.0. These results are explained on the basis of crystal field theory by considering the difference in the coordination states around uranium(V) in the two reductions.

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1. Introduction

Electron paramagnetic resonance (EPR) and optical spectra of uranium(V) species have been reported in both photo- and electrolytic reductions of several uranyl complexes in organic solutions [1,2]. These studies suggested that the coordination states around uranium(V) depend on the method of reduction and the type of counter-anions. In this study uranyl-TIBP (triisobutylphosphate) and uranyl-CMPO (octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide, which is one of the potential extractants for trivalent actinides and lanthanides) complexes with the counter-anions NO_3^- and ClO_4^- were prepared and both reduction processes of these four complexes were investigated. These observations will be published in detail elsewhere. This paper mainly reports the theoretical explanation of the results obtained experimentally based on crystal field theory.

2. Experimental details

2.1. Materials

Four kinds of complexes prepared were identified by elemental analysis as $UO_2(NO_3)_2 \cdot 2TIBP$, $UO_2(NO_3)_2 \cdot CMPO$, $UO_2(TIBP)_4(ClO_4)_2$ and $UO_2(CMPO)_3(ClO_4)_2$. ^{13}C and ^{31}P nuclear magnetic resonance (NMR) and IR spectra of these complexes revealed the participation of the oxygen atoms of both phosphoryl and carbonyl groups in the bonding to the central uranium(VI).

2.2. Measurements

Visible–near-IR spectral measurements were carried out during both photo- and electrolytic reductions and IR spectral measurements during the photoreduction. EPR spectra of TIBP, $CHCl_3$ and CH_3CN solutions were recorded on a JES-RE-2X spectrometer at −150 °C. Cyclic voltammograms were recorded with an NPOT-2501 potentiostat and an NPS-2 potential sweeper in an electrochemical cell using gold wires as the working electrode and counterelectrode.

3. Results and discussion

In the IR spectrum of $UO_2(NO_3)_2 \cdot CMPO$ the absorption bands assigned to $\nu(C{=}O)$, $\nu(P{=}O)$ and $\nu_3(UO_2)$ (asymmetric O–U–O stretch) are observed at 1589, 1140 and 933 cm^{-1} respectively before the photoreduction. After the photoreduction these absorption peaks shift to 1578, 1135 and 921 cm^{-1} respectively. These low wavenumber shifts are observed in all other complexes during the photoreduction. This means that the bond strength between uranium and oxygen of the carbonyl or phosphoryl groups in the equatorial plane becomes stronger and that between uranium and oxygen

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in the axial direction becomes weaker after the photoreduction.

Figure 1 shows the cyclic voltammograms for $UO_2(NO_3)_2 \cdot CMPO$ and $UO_2(CMPO)_3(ClO_4)_2$ in CH_3CN solution. As seen from the figures, the former is an irreversible reaction and the latter seems to be quasi-reversible. The observed peaks of the spectra in the visible–near-IR region which are assigned to uranium(V) are listed in Table 1. Broad EPR signals with g factors of about 2.15 are observed during the electrolytic reduction of all four sample solutions and during the photoreduction of $UO_2(TIBP)_4(ClO_4)_2$ and $UO_2(CMPO)_3(ClO_4)_2$ solutions. On the other hand, sharp EPR signals with g factors of about 1.97 are observed during the photoreduction of $UO_2(NO_3)_2 \cdot 2TIBP$ and $UO_2(NO_3)_2 \cdot CMPO$. As a result, the EPR signals observed in this work seem to be grouped into two types as shown in Table 1: one is the signal with a g factor greater than 2.0 and the other is the signal with a g factor less than 2.0. This tendency was also observed in the reduction of $UO_2(NO_3)_2 \cdot 2TBP$ [2].

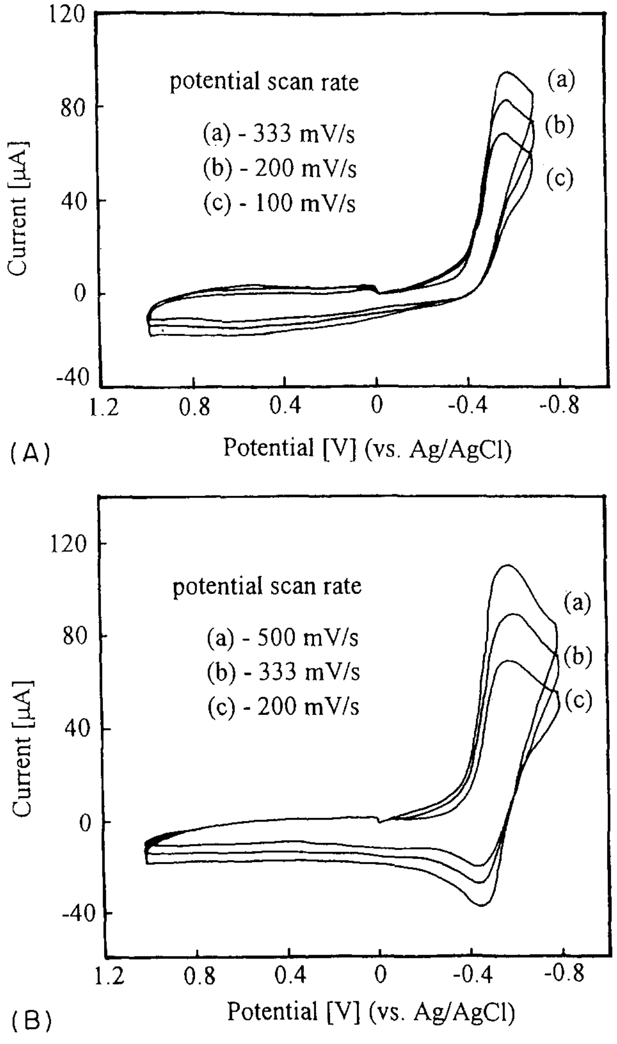

Fig. 1. Cyclic voltammograms of reduction of uranyl-CMPO complexes: A, $UO_2(NO_3)_2 \cdot CMPO$ (2 mM) in acetonitrile; B, $UO_2(CMPO)_3(ClO_4)_2$ (2 mM) in acetonitrile.

Why do the signals of uranylnitrate complexes depend on the method of reduction? In the electrolytic reduction process, uranylnitrate complexes with the counter-ion NO_3^- in the equatorial plane dissociate simultaneously upon accepting one electron from the cathode and the counter-ion NO_3^- is expelled from the equatorial plane. Therefore only organic ligands (TIBP or CMPO) exist in the equatorial plane after the electrolytic reduction. This state corresponds to the irreversible reaction observed in the voltammogram for $UO_2(NO_3)_2 \cdot CMPO$. In the photoreduction process, organic ligands such as TIBP or CMPO act as quenchers for the optically excited uranyl ion and uranium(V) is produced by an electron transfer through the quencher. Thus after the photoreduction of uranylnitrate complexes the nitrate ion still remains in the equatorial plane, resulting in the signals of type 2 listed in Table 1.

For uranylperchlorate complexes, both before and after electrolytic reduction, uranium has only organic ligands in the equatorial plane because of the absence of coordination ability of the perchlorate ion. Hence this electrode reaction is the reversible reaction as seen from the voltammogram for $UO_2(CMPO)_3(ClO_4)_2$. Moreover, during the photoreduction only organic ligands exist in the equatorial plane. Therefore uranylperchlorate complexes have signals of type 1 in both kinds of reduction.

4. Theoretical consideration based on crystal field theory

As shown in the IR spectra of uranyl complexes during the photoreduction, the bond between uranium and oxygen in the uranyl unit becomes weaker and in the equatorial plane the uranium–oxygen bond remains strong after the photoreduction. Therefore the symmetry of the crystal field around uranium(V) is assumed to be D_{4h} symmetry superimposed on octahedral symmetry. The hamiltonian $H_{D_{4h}}$ for D_{4h} symmetry is given as

$$H_{D_{4h}} = H_{O_h} + H_{\mathrm{dis}} \tag{1}$$

$$H_{\mathrm{dis}} = \frac{15}{4}\,\epsilon\alpha O_2^{\,0} + \frac{99}{8}\,\delta\beta O_4^{\,0} + \frac{560}{429}\,\eta\gamma O_6^{\,0} \tag{2}$$

where $O_n^{\,m}$ is the operator equivalent, α, β and γ are the multiplicative factors for the crystal field operator equivalent [3] and ϵ, δ and η are given by

$$\epsilon = \frac{4}{15}\,\frac{1}{2}\,\langle r^2\rangle e^2 Z_0\left(-\frac{2}{a^3} + \frac{2}{b^3}\right) \tag{3}$$

TABLE 1. Observed data of EPR and optical spectra of uranium(V) during photo- and electrolytic reductions

	Type 1	Type 2
Value of g factor Linewidth	$g>2.00$ (2.1–2.2) Broad (100–200 mT)	$g<2.00$ (1.96–1.98) Sharp (2–10 mT)
Peak pisitions in optical spectra (nm)	760–800, 920–940, 1020–1042, 1365–1415	760–800, 945–985, 1040–1055, 1330–1400
Photoreduction	$UO_2(TIBP)_4(ClO_4)_2$ $UO_2(CMPO)_3(ClO_4)_2$	$UO_2(NO_3)_2 \cdot 2TIBP$ $UO_2(NO_3)_2 \cdot CMPO$
Electrolytic reduction	$UO_2(TIBP)_4(ClO_4)_2$ $UO_2(CMPO)_3(ClO_4)_2$ $UO_2(NO_3)_2 \cdot 2TIBP$ $UO_2(NO_3)_2 \cdot CMPO$	

TABLE 2. Comparison of observed data of EPR and optical spectra with values calculated with parameters $\Theta = 5300$ cm^{-1}, $\Delta = 500$ cm^{-1} and spin–orbit coupling constant $\zeta = 1900$ cm^{-1}

	Type 1		Type 2	
	Found	Calculated	Found	Calculated
Value of ϵ (cm^{-1})	–	−1100	–	−700
Value of g factor	2.1–2.2	−2.16 ($g_{\parallel}$)	1.96–1.98	−1.97 ($g_{\parallel}$)
Energy levels (nm)	760–800	720	760–800	771
	920–940	960	945–985	966
	1020–1042	1123	1040–1055	1078
	1365–1415	1535	1330–1400	1493

etc., where a and b are the bond lengths between uranium and oxygen in the equatorial plane and in the axial direction respectively. The parameters δ and η are smaller than the parameter ϵ by about two orders, so we can ignore the parameters δ and η in the calculation. The difference between D_{4h} symmetry and O_h symmetry can be indicated by only the parameter ϵ. Eqn. (3) shows that when ϵ is larger than zero, the bond length between uranium and oxygen in the axial direction is shorter than that between uranium and oxygen in the equatorial plane, and vice versa. Therefore the coordination behaviour around uranium(V) can be elucidated by the parameter ϵ obtained from fitting experimental data. Taking observed values of the g factor and the four optical absorption peaks into account, a numerical analysis by changing the crystal field parameters Θ and Δ and the perturbation parameter ϵ was performed to get the best fit, keeping the spin–orbit coupling constant as 1900 cm^{-1}. The values with the best fit are listed in Table 2 and the energy levels are shown as a function of ϵ in Fig. 2.

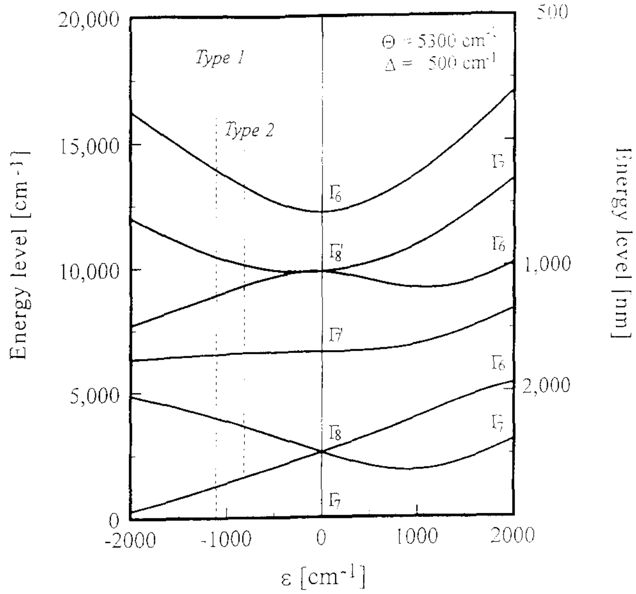

Fig. 2. Dependence of energy levels of uranium(V) in D_{4h} symmetry on value of ϵ.

The fact that two kinds of parameter ϵ are obtained suggests that the coordination states around uranium(V) produced in the two reductions can be grouped into two types. Type 1 represents uranium(V) with the only organic ligands in its equatorial plane and type 2 corresponds to uranium(V) with the organic ligand and the counter-ion (NO_3^-). It is noteworthy that in both kinds of reduction the bond lengths between uranium(V) and oxygen in the equatorial plane are shorter than those between uranium(V) and oxygen in the axial direction, because the parameter ϵ is smaller than zero. Moreover, it was found that the parameter ϵ obtained in type 1 is smaller than that obtained in type 2, so the bond between uranium(V) and the organic ligand is stronger than that between uranium(V) and the counter-ion (NO_3^-) in the equatorial plane.

The following general conclusions can be drawn from the measurements of EPR, optical spectra and cyclic voltammograms and the consideration based on crystal field theory.

(1) The mechanism of electrolytic reduction of the complexes differs depending on the type of counter-anion (NO_3^- or ClO_4^-).

(2) During the photoreduction of the complexes the substitution of the coordinated NO_3^- by an organic ligand does not occur.

(3) As a result of (1) and (2), the coordination behaviour around the uranium(V) species is grouped into two types as elucidated in the present paper.

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