ESR and Magnetic Susceptibility Evidence of Thermally Accessible Electron Transfer between $U^{5+}Cl_5[\phi_3P]$ and $U^{4+}Cl_5[\phi_3P]^{+\cdot}$

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(Received March 23, 1989)

Abstract

Magnetic susceptibility (χ) and electron spin resonance (ESR) absorption measurements have been carried out on powdered samples of $UCl_5[\phi_3P]$. The observed χ shows unusual values over two times as large as those of normal pentavalent uranium complexes. An ESR signal assignable to U^{5+} in $U^{5+}Cl_5$-$[\phi_3P]$ ($g = 1.2(4)$) and a signal with $g = 2.1(2-4)$ were observed. From the behavior of these signals with temperature, an intramolecular electron transfer equilibrium expressed by the equation, $U^{5+}Cl_5$-$[\phi_3P] \rightleftharpoons U^{4+}Cl_5[\phi_3P]^{+\cdot}$, was postulated, the left side of the equation being stable at lower temperatures. The observed χ could be well explained by considering contributions from both sides of the equation and the dependence of the relative contributions on temperature gave the value of ΔH of this equilibrium to be 0.032 Kcal/mol. Thus, it is concluded that an intramolecular electron transfer between uranium and phosphorus in $UCl_5[\phi_3P]$ can be thermally accessible.

Introduction

In order to have a deeper understanding of 5f electrons in actinide--metal ion complexes and/or compounds, pentavalent uranium, U^{5+}, is a suitable system due to its simple electron configuration of $[Rn]5f^1$, which can enable us to compare the experimental observation with the theoretical estimates without any consideration for an electron-correlation interaction. However, there are only a few reports on the complexes containing U^{5+} because of its instability under usual conditions. The present authors have directly observed an electron spin resonance (ESR) signal of pentavalent uranium intermediates in photo- and electrolytic reduction

processes of uranyl complexes in organic solutions [1].

Recently, transition metal complexes with substituted phosphines as ligands have been of interest in intramolecular electron transfer phenomena between the metal ion and phosphorus [2]. For uranium, there are a few reports about complex formation between uranium and substituted phosphine ligands, along with the value of $g = 2$ observed by ESR absorption spectra [3], but a study about the interaction between uranium and phosphorus has not yet been reported.

In the present study the magnetic susceptibility of the powdered uranium(V)pentachloride−triphenylphosphine complex, $UCl_5[\phi_3P]$, was measured from room temperature to 4.2 K and its ESR measurement was carried out from room temperature to 77 K. The observed results obtained by both measurements were analyzed consistently with each other, leading to a thermally accessible electron transfer equilibrium between uranium and phosphorus.

Experimental

Preparation of UCl5[φ3P]

Since pentavalent uranium complexes are extremely sensitive to atmospheric oxygen and moisture, all the preparation procedures were performed in the reaction vessel made of glass as shown in Fig. 1. Before the reaction started, the reaction vessel was evacuated to remove atmospheric oxygen and moisture and then dry argon gas was introduced into the vessel. UCl_5tcac (tcac is trichloroacrylylchloride, $Cl_2C=CClCOCl$) was prepared in this vessel and dissolved in benzene. The tube containing this solution was removed from the reaction vessel by using the rubber tube and immediately put into a dry box filled with argon gas. A slight excess of triphenylphosphine in benzene degassed before use was added to this solution. Then a pale greenish complex

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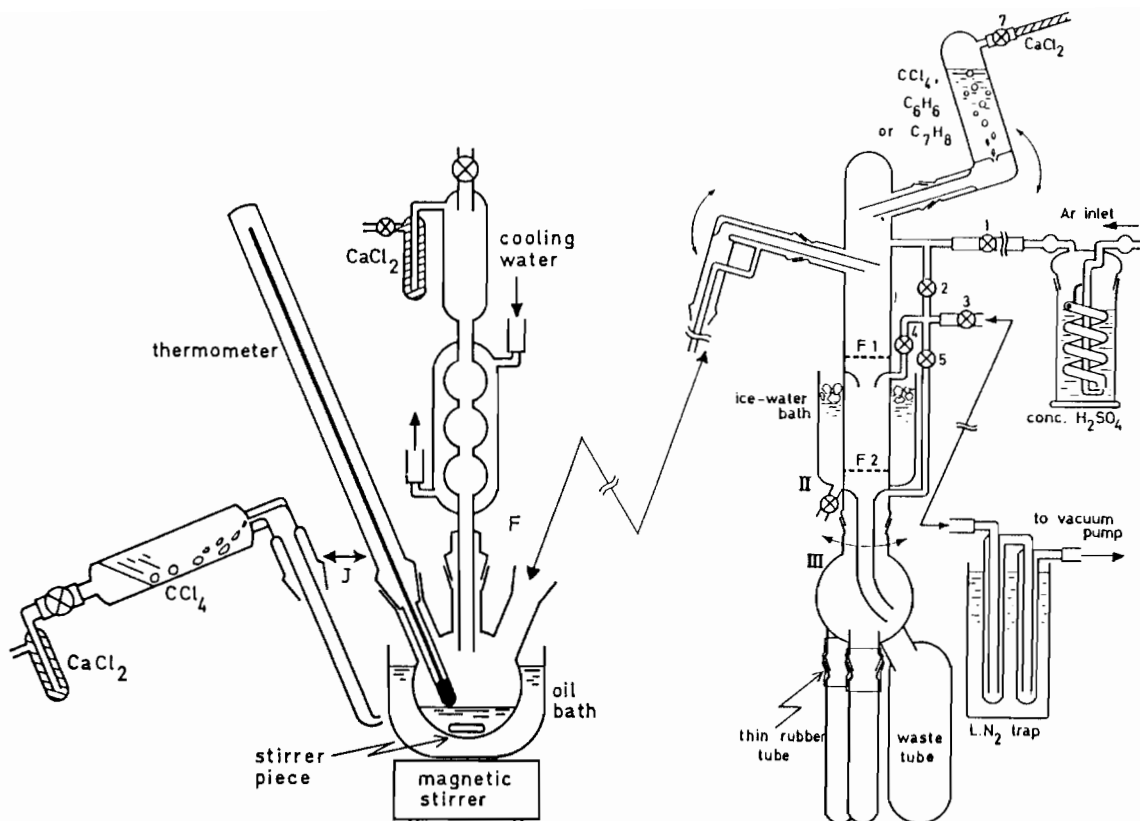
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Fig. 1. Apparatus. J: after completing the reaction the thermometer is replaced by the reservoir of CCl_4.

precipitated immediately. After stirring 30 min, the precipitates were washed several times with benzene, vacuum-dried overnight and sealed into quartz tube under vacuum for the magnetic measurements. The preparation procedure was described in detail elsewhere [4].

Analysis

The uranium content was determined gravimetrically by an ammonium method [5], while the chlorine content was determined by potentiometric titration with a standard silver solution. Hydrogen and carbon contents were determined with a Yanagimoto CHN coder MT-2. *Anal.* Calc. for UCl_5-$[\phi_3P] \cdot \frac{2}{3}C_6H_6$, $C_{22}H_{19}PCl_5U$: C, 36.19; H, 2.60; Cl, 24.33; U, 32.63. Found: C, 36.84; H, 2.77; Cl, 25.34; U, 33.21%.

Physical Measurements

The measurement of magnetic susceptibility was carried out on the powdered sample sealed into a quartz tube by the Faraday method from room temperature to 4.2 K. $HgCo(NCS)_4$ [6] was used as a calibrant of the susceptibility. In order to confirm that the sample was free from a ferromagnetic impurity, the dependence of the magnetic susceptibility on the intensity of the magnetic field was measured

in the range from 0.1 to 1 T. The value of the magnetic susceptibility observed was corrected for the diamagnetic susceptibility of $UCl_5[\phi_3P] \cdot \frac{2}{3}C_6H_6$ ($-322.80 \ 10^{-6}$ cgs emu/mol) and that of the quartz tube.

The ESR spectra were recorded on a JES-ME-2X spectrometer from room temperature to 77 K. The g value was determined with reference to the signal of the manganese ions doped in MgO.

$UCl_5[\phi_3P]$ was very sensitive to oxygen and moisture in air. Normal paper filters could not be used for the filtration of the solution containing U^{5+} since the water and oxygen molecules adsorbed on the paper react rapidly with the complex. Even the surface of the glass vessel gave rise, at first, to the disproportionation reaction of the solution contacted to the surface. Therefore, we could not measure the absorption spectra. Diffuse reflectance spectra were recorded on a HITACHI EPS-3T recording spectrophotometer at room temperature.

Results and Discussion

The magnetic susceptibility of $UCl_5[\phi_3P]$ is shown in Fig. 2 along with those of UCl_5 [7] and UCl_5tcac [4]. The paramagnetic susceptibility of UCl_5 and
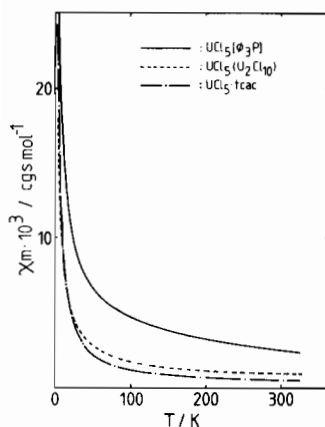
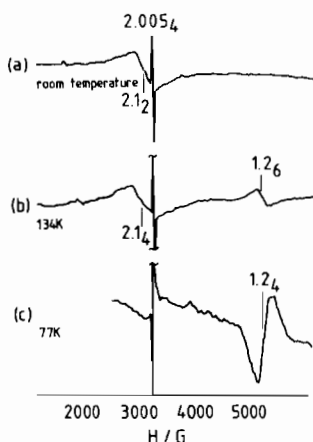Fig. 2. Temperature dependence of magnetic susceptibilities for $UCl_5[\phi_3P]$ (——), UCl_5 (- - - -) and UCl_5tcac (—·—).

Fig. 3. Changes of X-band ESR spectra of powdered UCl_5-$[\phi_3P]$ at room temperature (a), 134 K (b) and 77 K (c). The effective *g* values are given.

UCl_5tcac is a prototype of U^{5+} complexes and can be simply explained based on a crystalline field theory for $^2F_{5/2}$ of a $5f^1$ configuration of U^{5+}. However, the magnitude of magnetic susceptibility of the present sample is very large compared with the others and cannot be explained, in principle, by taking only U^{5+} into account.

Figure 3(a)–(c) shows the ESR absorption spectra of $UCl_5[\phi_3P]$ at room temperature, 134 K and 77 K, respectively. There are three kinds of paramagnetic species responsible for ESR, as seen in the Figure. The sharp signal at the center of the spectra can be easily assigned as an organic radical from its linewidth of 24 gauss and the *g* value of 2.005 ((a), (b) and (c)). These values correspond to those of the organic free radicals, as was already observed by Selbin *et al.* [3]. The most probable candidate of these radicals is $[\phi_3P]^{+\cdot}$ derived from $UCl_5[\phi_3P]$. Berclaz and Geoffroy reported the ESR data of $[\phi_3P]^{+\cdot}$ formed in single crystal ϕ_3PBCl_3 by X-ray irradiation. The

isotropic *g* value was 2.004 [8]. The *g* values of other P-centered cation radicals are in the range of 2.004 to 2.008 with large hyperfine splitting. By comparing our data with these values, it is appropriate to conclude that the free radical under consideration is a P-centered radical such as $[\phi_3P]^{+\cdot}$. The existence of such a free radical in $UCl_5[\phi_3P]$ indicates that a redox reaction in the sample occurs in a small amount.

$$UCl_5[\phi_3P] \rightleftharpoons UCl_4 + Cl[\phi_3P]^{+\cdot}$$
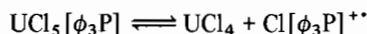
Free radicals of the type $P^{+\cdot}$ generally show the hyperfine splitting of about a few hundreds gauss due to the nuclear spin of ^{31}P with $I = 1/2$ in solution and solid solution. In the condensed magnetic materials, however, such hyperfine splitting coalesces into a single line in the presence of an exchange interaction [9]. The present signal with linewidth of about 24 gauss without the hyperfine splitting might be due to the strong exchange interaction with neighboring paramagnetic species, such as U^{4+} and U^{5+}.

The broad signal in the higher magnetic-field side observed at 77 K becomes weaker at 134 K and finally disappears at room temperature. This signal is attributable to U^{5+} in $U^{5+}Cl_5[\phi_3P]$ with respect to its linewidth of 250 gauss and *g* value of 1.2(4). The $5f$ electron of U^{5+} is very sensitive to the environmental condition in the crystal. The ESR signal of U^{5+} is in general more observable than that of U^{4+} but the condition for the observation is limited to, for example, substances like an insulator [10]. Disappearance of this signal at room temperature is caused by a reduction of concentration as described later or a fast relaxation mechanism encountered sometimes in U^{5+}. The value of the present *g* value, 1.2(4), is the upper limit in the range of the values estimated from the distorted octahedral crystalline field around U^{5+} [4].

The observed ESR signal with *g* value of 2.005(4) in this experiment is very weak in intensity. This species probably comes from the decomposition of the molecule, $UCl_5[\phi_3P]$. This can be detectable in ESR but is negligibly responsible for the magnetic susceptibility. However, its existence is a definite key in the analysis of the ESR spectra. The broad signal at about $g = 2.1(2–4)$ becomes stronger with increasing temperature ((a), (b) and (c)). In Fig. 4 the observed intensity changes of the ESR signal of $g = 2.1(2–4)$ and that of $U^{5+}Cl_5[\phi_3P]$ are plotted as functions of temperature. This signal is considered to be due to a complex, $U^{4+}Cl_5[\phi_3P]^{+\cdot}$, produced by the reversible intramolecular electron transfer as described in the following section. If this complex, $U^{4+}Cl_5[\phi_3P]^{+\cdot}$, has a magnetic interaction among spins of U^{4+} and $[\phi_3P]^+$, a coalesced broad signal may appear. The fact that the ESR intensity at $g = 2.1(2–4)$ increases, with increasing temperature, and that of $U^{5+}Cl_5[\phi_3P]$ decreases concomitantly suggests the coexistence of these species in an equilibrium.
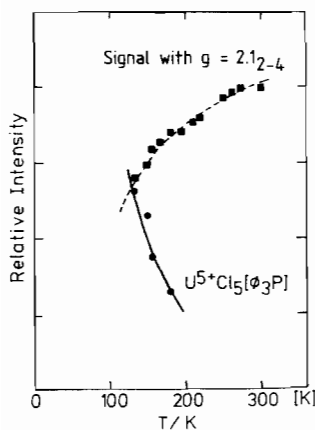
Fig. 4. Temperature dependence of relative intensities of ESR signals observed for $U^{5+}Cl_5[\phi_3P]$ (●) and with $g = 2.1(2-4)$ (■).

The electronic spectra of U^{4+} and U^{5+} are sensitive to a change in the circumstances. In our experience, U^{5+} in the form of UO_2^+ appearing in the reduction processes of UO_2^{2+} species by photo or electrolytic reductions is greenish blue, absorption appearing at about 780 nm [1]. On the other hand, UCl_5 has a red–brown–violet color [7]. Thus, the color of the U^{5+} species depends on the nature of chemical bond. The U^{4+} in UCl_4 species is greenish and those in $U(acac)_4$ species are brown according to the nature of the chemical bond [11]. In the diffuse reflectance spectra of the present sample, the broad and weak absorption peaks at $16\,770$ and $15\,810$ cm^{-1} with a shoulder at $12\,200$ cm^{-1} could be detected at room temperature. The two former absorptions can be attributed to the U^{4+} complex in comparison with absorption peaks at $16\,760$ and $15\,100$ cm^{-1} observed for $UCl_4(\phi_3P=O)_2$ in solid reflection spectra [12]. The latter shoulder at $12\,200$ cm^{-1} can be assigned to the U^{5+} complex compared with the absorption peak at $11\,850$ cm^{-1} for $UCl_5\phi_3PO$ in CH_2Cl_2 solution [13].

Previously we successfully interpreted ESR and magnetic susceptibility evidence of thermally accessible electron-transferred species in $U_2Cl_{10}[\phi_3As]$ [14]. In order to interpret the results mentioned above, we also introduce here a reversible electron transfer equilibrium described by eqn. (1), taking into account the value of magnetic susceptibility and an unusual temperature behavior of the ESR signals

$$U^{5+}Cl_5[\phi_3P] \rightleftharpoons [U^{4+}Cl_5][\phi_3P]^{+\cdot} \qquad (1)$$
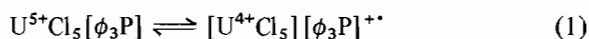
The left-hand side of eqn. (1) shows the state of this complex in the low temperature region and the right-hand side shows the state of this complex in the higher temperature region. The complex in the right-hand side irreversibly dissociates further into $U^{4+}Cl_4$ and $Cl[\phi_3P]^{+\cdot}$ in so small a degree that their contribution to the magnetic susceptibility is negligibly

small, although in the ESR spectra the latter signal is observable.

In this reversible electron-transfer equilibrium system the paramagnetic species are U^{5+}, U^{4+} and the triphenylphosphine cation radical. Magnetic susceptibilities of these three paramagnetic species are calculated at first as follows. Although the crystal structure of $UCl_5[\phi_3P]$ has not yet been elucidated, the symmetry of the crystalline field around the central uranium ion is reasonably assumed from its chemical formula to be basically octahedral as in the case of UCl_5tcac. When the octahedral crystalline field is distorted by the introduction of different kind of ligands and the symmetry lowers to tetragonal, the first excited state Γ_8 splits into Γ_6 and Γ_7 [15] in U^{5+} with $[Rn]5f^1$ configuration. The solid circles in Fig. 5 are the values of the magnetic susceptibility of U^{5+} calculated by taking into account the ground state Γ_7 and the first excited state Γ_6 split from Γ_8 with the difference of 1780 cm^{-1}.

It is well known that U^{4+} with the ground term of $^3H_4$ has no magnetic moment but only a very small temperature independent paramagnetism in the crystalline field with octahedral symmetry [16]. But under a tetragonal crystalline field, the first excited state Γ_4, splits into Γ_2 and Γ_5. The calculated values of magnetic susceptibility from the ground state and the first excited state are plotted as open squares in Fig. 5, having a difference in energy of about 320 cm^{-1} between the two states Γ_1 and Γ_5 [12]. We have tried to fit the calculated susceptibility data consisting of U^{4+} and U^{5+} to the experimental data, but any combination of the parameters mentioned above could not reproduce the experimental data: the calculated values are very small in the low temperature range, even if the room temperature value was reproduced.

In the right-hand side of the equilibrium of eqn. (1) there are two paramagnetic species, the triphenylphosphine cation radical and U^{4+}. Then the paramagnetic susceptibility of the right-hand side is
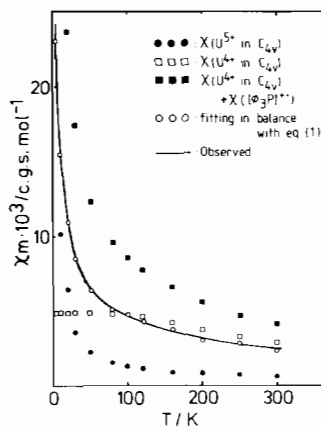

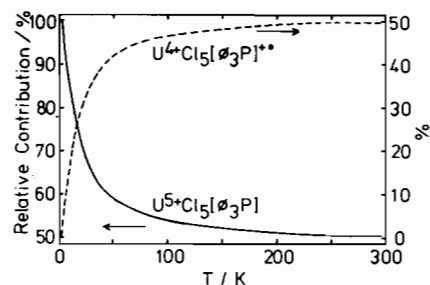Fig. 5. Temperature dependence of magnetic susceptibilities.

Fig. 6. Temperature dependence of relative contributions from $U^{5+}Cl_5[\phi_3P]$ (——) and $U^{4+}Cl_5[\phi_3P]^{+\cdot}$ (- - - -) obtained by fitting magnetic susceptibility.

expressed by the summation of the magnetic susceptibility of U^{4+} and that of the cation radical which can be obtained by assuming Curie's law (solid squares in Fig. 5). Finally, the observed solid line can be nicely fitted by considering the contributions from the paramagnetic species of both sides in balance in the electron transfer equilibrium. Figure 6 shows the relative contribution from both sides with a good fit to the experimental data in Fig. 2. The contribution from the left side reaches close to 100 percent as the temperature decreases while at room temperature the ratio of contributions from both sides is equal to about 1:1. The enthalpy change of this electron transfer equilibrium can be estimated to be 0.032 Kcal/mol (135 J/mol) from the dependence of the obtained equilibrium constant on temperature.

Further, it should be noted that when we apply the intramolecular equilibrium described in the present paper to the explanation of the experimental results reported by Selbin *et al.*, their data such as the value of the *g* factor, the magnetic susceptibilities, etc. can be explained consistently.

Concerning the electron spin resonance spectra, the proposed electron transfer equilibrium can, of course, explain the behavior of the ESR absorption spectra with temperature. Thus it is concluded that an intramolecular electron transfer between the metal ion (uranium) and its ligand (phosphine) is also thermally accessible in $UCl_5[\phi_3P]$ in addition to the case in $U_2Cl_{10}[\phi_3As]$ published previously.

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