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Investigation of charge-transfer absorptions in the uranyl UO_2^{2+}(VI) ion and related chemical reduction of UO_2^{2+}(VI) to UO_2^{+}(V) by UV–Vis and electron paramagnetic resonance spectroscopies

Xiaoping Sun [a,*], Derrick R.J. Kolling [b], Hajer Mazagri [a], Blake Karawan [a], Courtney Pierron [a]

[a] Department of Natural Sciences and Mathematics, University of Charleston, Charleston, WV 25304, USA
[b] Department of Chemistry, Marshall University, Huntington, WV 25755, USA

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ABSTRACT

The uranyl UO_2^{2+}(VI) cation (hydrated) exhibited strong charge-transfer absorptions at 350–400 nm in aqueous solutions containing bromide and iodide. The charge-transfer absorptions originate from a single-electron transfer from a halide anion to the uranium(VI) valence shell. Their intensities (represented by absorbance at 375 nm) were found to be directly proportional to molar concentrations of the halide (bromide or iodide) and UO_2^{2+} in solution, respectively, showing the nature of a bimolecular interaction in the charge-transfer absorption transition. The absorptions were also greatly enhanced by sulfuric acid, and their intensity (absorbance at 375 nm) increased linearly as a function of the acid molarity. An electron paramagnetic resonance (EPR) study has indicated that the charge-transfer also took place slowly in the dark, resulting in appreciable thermal chemical reduction of diamagnetic UO_2^{2+}(VI) (hydrated) to paramagnetic UO_2^{+}(V) (hydrated) (g = 2.08) by bromide and iodide. In the presence of sulfuric acid, CH_3SOCH_3 (DMSO) was shown by EPR to undergo a charge-transfer oxidation by UO_2^{2+}(VI) to a stable CH_3SOCH_2 ($DMSO^{\cdot}$) radical (singlet, g = 2.01), and UO_2^{2+}(VI) was reduced to UO_2^{+}(V). A possible mechanism for this oxidation–reduction has been proposed. The charge-transfer absorption transition (350–400 nm) between UO_2^{2+}(VI) and phenol (PhOH) in acetone was observed and characterized. A chemical oxidation–reduction of UO_2^{2+}(VI) [in the form of $U^{VI}O_2(acetone)_5^{2+}$] and PhOH in acetone was found by EPR to give UO_2^{+}(V) [in the form of $U^{V}O_2(acetone)_5^{+}$] and a stable phenoxyl ($PhO^{\cdot}$) radical (singlet, g = 2.00) via a simultaneous charge-transfer and deprotonation pathway.

1. Introduction

The linear uranyl UO_2^{2+}(VI) ion ($D_{\infty h}$ symmetry), a major form of uranium(VI), exhibits diverse chemistry. This is mainly because the central uranium atom in UO_2^{2+} is readily coordinated by many anionic and electrically neutral ligands in its equatorial positions [1–9]. In addition, uranium possesses a few known oxidation states including U(VI), U(V), and U(IV) [10]. Thus, reduction of UO_2^{2+}(VI) to the lower oxidation states of uranium forms another interesting aspect of its chemistry. Of these oxidation states, U^{4+} can readily precipitate out as $U(OH)_4$ in neutral or weakly basic aqueous media [10], facilitating removal of radioactive waste (uranium) from the water system. Studying chemical speciation of UO_2^{2+} in both aqueous and non-aqueous solutions by electronic and molecular spectroscopies and theoretical calculations has received much attention [11–19]. As part of the efforts made in this area of research, we have characterized vibronic structures of the excited state of UO_2^{2+} in various media containing strong acids and different coordinating ligands [18,19]. More recently, we have studied the behavior of UO_2^{2+} in media containing reductive halides (Br^- and I^-), phenol (PhOH), and dimethyl sulfoxide (DMSO) by electronic absorption (UV–Vis) spectroscopy. We identified charge-transfer absorptions of UO_2^{2+}(VI) in these media. Following the UV–Vis spectroscopic studies, we investigated chemical reduction (in the dark) of UO_2^{2+}(VI) to UO_2^{+}(V) with bromide, iodide, phenol, and DMSO by electron paramagnetic resonance (EPR) spectroscopy. The results have provided further evidence to support the general charge-transfer pathway for UO_2^{2+}(VI) reduction.

Although uranium(VI) has received much investigation, the studies of uranium(V) are rare mainly due to its relative instability [10]. Previously, UO_2^{2+}(VI) (diamagnetic) has been found to undergo photochemical and electrolytic reduction to UO_2^{+}(V) (paramagnetic), which was characterized by low-temperature EPR spectroscopy showing a broad signal in solution with the g-factor being slightly greater than 2 [20,21]. In addition, laser flash photolysis of UO_2^{2+}

* Corresponding author. Tel.: +1 304 357 4898; fax: +1 304 357 4715.
E-mail address: xiaopingsun@ucwv.edu (X. Sun).

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has been performed in the aqueous media containing reductive bromide, iodide, and 4-chlorophenol [22,23]. The spectroscopic data of the research suggested oxidation–reduction processes taking place via the $(UO_2^{2+})^*$ excited state. However, up-to-date investigation on direct thermal chemical reduction of UO_2^{2+} by halides, phenol and DMSO in the dark has not been reported prior to our present work. We now report our new findings.

2. Experimental

The electronic absorption (UV–Vis) spectra were recorded throughout this work using a UV-1601 Shimadzu spectrophotometer which is connected to a Dell computer equipped with Shimadzu UV Probe (Ver. 2.21) software. The instrument consists of a light source, a sample chamber, a diode-array detector, and a data acquisition computer. The sample was placed between the light and the detector. The data acquisition computer then measured the amount of ultraviolet or visible light that passed through the sample at varying wavelengths. The data were processed using the Shimadzu UV Probe software installed in the Dell computer.

The Bruker EMXplus EPR spectrometer with microwave frequency 9.37 GHz (X-band) was used for the EPR measurement throughout this work. All spectra were recorded at the liquid nitrogen temperature (~80 K), with microwave power of 5 mW, a modulation amplitude of 15 G, and a modulation frequency of 100 kHz.

Uranyl(VI) nitrate hexahydrate $[UO_2(NO_3)_2\text{-}6H_2O]$, obtained from Sigma–Aldrich Chemical Company, was used as the source of uranyl(VI) ion (UO_2^{2+}) (unless otherwise specified). In the experiment conducted in each of all the media as specified throughout the work, the $UO_2(NO_3)_2\text{-}6H_2O$ solid was dissolved in the corresponding medium with specific composition at ambient conditions. A UV–Vis cell (with path length of 1 cm) was then filled with each of the UO_2^{2+} solutions, and an electronic absorption (UV–Vis) spectrum was recorded. For EPR measurements, a uranyl solution with specific composition was added into a 4 mm quartz tube which was subsequently placed in the cavity of the spectrometer. The EPR spectra were recorded at ~80 K with the cavity background subtracted.

3. Results and discussion

3.1. Charge-transfer absorption transition between uranyl(VI) and halides (Br^- and I^-)

Fig. 1a shows the UV–Vis absorption spectra of UO_2^{2+} (0.10 M) in the neutral aqueous media that contained different concentrations of NaBr (0–6.0 M). The bottom curve (#1) is the spectrum of UO_2^{2+} in water ($[Br^-] = 0$ M) with the maximum absorption being at 410 nm (the UO_2^{2+} π–π^* transition [11,18]). As the molar concentration of bromide in solution increased gradually to 6.0 M (from bottom to top), the intensity of the absorption in the higher-energy side (350–400 nm) of the spectra was enhanced dramatically. As a result, when the concentration of Br^- reached the range of 3.6–6.0 M [the top four spectra (#5–8) in Fig. 1a], the initial π–π^* absorption band of UO_2^{2+} centered at 410 nm gradually disappeared. Such a structural change in the UO_2^{2+} absorption band was affected more remarkably by KI (Fig. 1b). Fig. 1b shows progression of the UO_2^{2+} (0.10 M) spectra in the KI (aq) media as a function of the molar concentration of iodide in solution. When the I^- concentration reached only 0.80 M (the top spectrum #4), the initial π–π^* absorption band of UO_2^{2+} was mostly blurred due to strong enhancement of the absorption of UO_2^{2+} at 350–400 nm. The quantitative relationships between the intensity of the absorptions of UO_2^{2+} (0.10 M) in the halides (bromide and iodide) solutions, reasonably represented by the absorbance at 375 nm (A_{375}), and the molar concentrations of the halides (bromide and iodide, respectively) are displayed in Fig. 1. For both bromide and iodide solutions of uranyl(VI) in which UO_2^{2+} was maintained at a constant concentration (0.10 M), A_{375} is directly proportional to molar concentration of the halide, showing the involvement of Br^- and I^- in the strong absorptions at 350–400 nm.

Analogous to Figs. 1, 2a and b show the UV–Vis absorption spectra of uranyl(VI) at different concentrations in the aqueous solutions containing 4.0 M NaBr and 0.50 M KI, respectively. Strong absorptions at 350–400 nm were identified from all the spectra. As the concentrations of bromide and iodide in the solutions were maintained at the constant levels, A_{375} were shown in Fig. 2a and b to be proportional to molar concentrations of UO_2^{2+} in the solutions.

The strong absorptions at 350–400 nm in the UO_2^{2+} spectra which were effected by bromide (Fig. 1a) and iodide (Fig. 1b) are characteristic of charge-transfer absorption transitions between uranyl(VI) and bromide and between uranyl(VI) and iodide, respectively. Each of them originates from a single-electron transfer from a reductive halide (Br^- or I^-) to the uranium(VI) valence shell as shown in Eq. (1).

$$:\ddot{X}:^- + U^{VI}O_2(H_2O)_n^{2+} \xrightarrow[350\text{-}400\ nm]{h\nu} \left[:\ddot{X}\cdot, U^{V}O_2(H_2O)_n^{+}\right] \quad (1)$$

(X = Br or I, n = 3-5)

In the aqueous media both UO_2^{2+}(VI) and UO_2^{+}(V) ions are coordinated by 3–5 water molecules in the equatorial positions of the central uranium. The charge-transfer transition results in reduction of uranium(VI) to uranium(V) and oxidation of a halide to a halogen radical. Once generated, the halogen radical and UO_2^{+}(V) [in the form of $U^VO_2(H_2O)_n^+$, n = 3–5] may initially form an ion-radical pair. The linear relationships of the intensity of the charge-transfer absorption (A_{375}) of UO_2^{2+}(VI) in the bromide or iodide solution with the halide concentration and with the uranyl(VI) concentration have clearly demonstrated the nature of a bimolecular (intermolecular) interaction between halide and UO_2^{2+} [in the form of $U^{VI}O_2(H_2O)_n^{2+}$, n = 3–5] in the charge-transfer absorption transition as shown in Eq. (1).

At a given concentration, a more reductive anion (with lower standard reduction potential) has stronger ability to drive the charge-transfer occur. This accounts for the observation (by comparison of Fig. 1a and b) that at a given concentration of halides the intensity of charge-transfer absorption of UO_2^{2+} in the solution of iodide (a more reductive anion with lower standard reduction potential) is greater than in the solution of bromide (a less reductive anion with higher standard reduction potential). We also recorded UV–Vis spectra of UO_2^{2+} (0.10 M) in the aqueous solutions