**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-visible and
Electron Paramagnetic Resonance Spectroscopies**

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Abstract

The uranyl $\text{UO}_2^{2+}(\text{VI})$ 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 $\text{UO}_2^{2+}(\text{VI})$ (hydrated) to paramagnetic $\text{UO}_2^+(\text{V})$ (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 $\text{UO}_2^{2+}(\text{VI})$ to a stable $\text{CH}_3\text{SOCH}_2^\bullet$ (DMSO $^\bullet$) radical (singlet, $g=2.01$), and $\text{UO}_2^{2+}(\text{VI})$ was reduced to $\text{UO}_2^+(\text{V})$. A possible mechanism for this oxidation-reduction has been proposed. The charge-transfer absorption transition (350-400 nm) between $\text{UO}_2^{2+}(\text{VI})$ and phenol (PhOH) in acetone was observed and characterized. A chemical oxidation-reduction of $\text{UO}_2^{2+}(\text{VI})$ [in the form of $\text{U}^{\text{VI}}\text{O}_2(\text{acetone})_5^{2+}$] and PhOH in acetone was found by EPR to give $\text{UO}_2^+(\text{V})$ [in the form of $\text{U}^{\text{V}}\text{O}_2(\text{acetone})_5^+$] and a stable phenoxyl (PhO $^\bullet$) radical (singlet, $g=2.00$) via a simultaneous charge-transfer and deprotonation pathway.

Keywords: Uranyl / Spectra / Charge-transfer / Oxidation-reduction / EPR / UV-vis / Radical

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 $\text{U}(\text{OH})_4$ 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 behaviour of UO_2^{2+} in media containing reductive halides (Br^- and I^-), phenol (PhOH), and dimethyl sulfoxide (DMSO) by electronic absorption (UV-visible) spectroscopy. We identified charge-transfer absorptions of UO_2^{2+} (VI) in these media. Following the UV-visible 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+} 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 $(\text{UO}_2^{2+})^*$ 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-visible) 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 $[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, 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 $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solid was dissolved in the corresponding medium with specific composition at ambient conditions. A UV-visible cell (with path length of 1 cm) was then filled with each of the UO_2^{2+} solutions, and an electronic absorption (UV-visible) 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^-)

Figure 1a shows the UV-visible 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 ($[\text{Br}^-] = 0 \text{ M}$) 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 Figure 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 (Figure 1b). Figure 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 Figure 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 Figure 1, Figure 2a and Figure 2b show the UV-visible 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 Figure 2a and Figure 2b 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 (Figure 1a) and iodide (Figure 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 Equation 1.

In the aqueous media both $\text{UO}_2^{2+}(\text{VI})$ and $\text{UO}_2^+(\text{V})$ 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 $\text{UO}_2^+(\text{V})$ [in the form of $\text{U}^{\text{V}}\text{O}_2(\text{H}_2\text{O})_n^+$, $n = 3-5$] may initially

form an ion-radical pair. The linear relationships of the intensity of the charge-transfer absorption (A_{375}) of $\text{UO}_2^{2+}(\text{VI})$ 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 $\text{U}^{\text{VI}}\text{O}_2(\text{H}_2\text{O})_n^{2+}$, $n = 3-5$] in the charge-transfer absorption transition as shown in Equation 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 Figure 1a and Figure 1b) 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-visible spectra of UO_2^{2+} (0.10 M) in the aqueous solutions containing NaCl. No charge-transfer absorption was observed as the concentration of NaCl varied from 0–6 M essentially due to the relatively low reducing ability of chloride (high standard reduction potential).

Figure 3 shows the UV-visible spectra of UO_2^{2+} (0.10 M) in the 3.0 M NaBr aqueous solutions that contained 0.50–3.0 M sulfuric acid. All the spectra exhibited strong charge-transfer absorptions at 350–400 nm due to the single-electron transfer between bromide and uranyl(VI) as described in Equation 1. The intensity of the charge-transfer absorption (A_{375}) increased linearly as a function of the acid concentration as shown from the plot in Figure 3. Most likely, this is because that a strong acid disfavors and partially prevents coordination of water molecules to the central uranium atom in uranyl(VI). Consequently, the uranium center can be contacted by more Br^- anions, equivalent to increase in the bromide concentration in the surrounding area to the uranium center.

Sarakha et.al. studied electron-transfer oxidation of 4-chlorophenol by the $(\text{UO}_2^{2+})^*$ excited state (photochemical oxidation) and found charge-transfer absorption of UO_2^{2+} in the aqueous media that contained reductive 4-chlorophenyl [23]. The observed spectral feature was similar to that in this work for uranyl(VI) in the Br^- and I^- solutions. In addition, Sun and his former coworkers have previously identified a related charge-transfer absorption in the arene- NS_2^+ complexes formed between the linear $[\text{S}=\text{N}=\text{S}]^+$ cation, structurally analogous to UO_2^{2+} , and electron-donating arenes [24].

3.2 Chemical Reduction of $\text{UO}_2^{2+}(\text{VI})$ to $\text{UO}_2^+(\text{V})$ by Br^- and I^-

The UV-visible spectra (Figure 4a) of a mixture of $\text{UO}_2^{2+}(0.10 \text{ M})$ and $\text{NaBr}(4.5 \text{ M})$ in the neutral aqueous solution did not exhibit substantial change over 47 h. This indicates that there was essentially no reaction between $\text{UO}_2^{2+}(\text{VI})$ and NaBr in the neutral condition. In the presence of sulfuric acid (2.0 M), $\text{UO}_2^{2+}(0.10 \text{ M})$ was found in this work to undergo slow, but appreciable thermal reduction with bromide (4.5 M) in the dark at ambient temperature over an extended period of time. The aqueous solution of $\text{UO}_2^{2+}(0.10 \text{ M})$ - $\text{NaBr}(4.5 \text{ M})$ - $\text{H}_2\text{SO}_4(2.0 \text{ M})$, 10–24 h after it was made, turned reddish-brown (Br_2), also with a small amount of brown vapor (Br_2) formed above the solution. Figure 4b shows that there was a dramatic increase in absorption in 350–400 nm after the reaction of $\text{UO}_2^{2+}(0.10 \text{ M})$ - $\text{NaBr}(4.5 \text{ M})$ - $\text{H}_2\text{SO}_4(2.0 \text{ M})$ had proceeded for 9 h. According to the study by Burrows [22], the increase in absorption in 350–400 nm is attributable to formation of the bromide(Br^-)–bromine($\text{Br}^\cdot$) anion-radical pair ($\text{Br}_2^{\cdot-}$). An analogous reaction mixture with the same composition (using uranyl acetate dihydrate as the source of UO_2^{2+}) was then (~24 h after it was prepared) characterized by EPR spectroscopy at 80 K (Figure 5). The EPR spectrum (Figure 5) shows a strong broad signal with $g=2.08$, attributable

to $\text{UO}_2^+(\text{V})$ by referencing to the previous studies [20,21]. The spectral data indicated that $\text{UO}_2^{2+}(\text{VI})$ [in the form of $\text{U}^{\text{VI}}\text{O}_2(\text{H}_2\text{O})_n^{2+}$, $n = 3-5$] had been reduced to $\text{UO}_2^+(\text{V})$ [in the form of $\text{U}^{\text{V}}\text{O}_2(\text{H}_2\text{O})_n^+$, $n = 3-5$] by Br^- thermally in the dark, presumably, via the charge-transfer (single-electron transfer) process formulated in Equation 1. At this stage (~24 h), it was found that the characteristic absorption of UO_2^{2+} centered at 410 nm disappeared from the UV-visible spectrum of the solution, indicating that the reduction of $\text{UO}_2^{2+}(\text{VI})$ to $\text{UO}_2^+(\text{V})$ was essentially complete. Simultaneously, Br^- was oxidized to the reactive $\text{Br}^\cdot$ radical, which subsequently associated with a preexisting bromide anion favorably in solution giving the more stable, long-lived anion-radical pair $\text{Br}_2^{\cdot-}$. When the concentration of bromide in solution is high (e.g. 4.5 M), a bromine radical center generated initially from the charge-transfer oxidation can be delocalized within many Br^- anions by forming such an anion-radical pair $\text{Br}_2^{\cdot-}$ reversibly. As a result, the radical is stabilized and observable by UV-visible spectroscopy.

Iodide has been shown much more reactive towards uranyl(VI). Figure 6a shows the UV-visible spectra of a mixture of $\text{UO}_2^{2+}(0.10 \text{ M})$ and $\text{KI}(0.5 \text{ M})$ in the neutral aqueous medium at different times after the mixture was prepared. Similar to uranyl(VI) in the medium containing bromide (Figure 4b), the spectra of $\text{UO}_2^{2+}(0.10 \text{ M})$ in $\text{KI}(0.5 \text{ M})$ exhibited gradual increase in absorption in 350-400 nm over time. In addition, the feature of the absorption band of the uranyl(VI) ion at 410 nm mostly disappeared after 26 h. According to Burrow's previous study [22], the increase in absorption at 350-400 nm in the spectra of the $\text{UO}_2^{2+}(0.10 \text{ M})$ - $\text{KI}(0.5 \text{ M})$ mixture (Figure 6a) is attributable to absorption of the iodide(I^-)–iodine($\text{I}^\cdot$) anion-radical pair ($\text{I}_2^{\cdot-}$). It is in the same wavelength range as that for the uranyl(VI)-iodide charge-transfer absorption.

Figure 6b shows the EPR spectrum (80 K) of a 0.10 M UO_2^{2+} (as the acetate salt) aqueous solution in the presence of KI (1 M) after UO_2^{2+} and KI were mixed for 24 hours and the solution turned dark brown (I_2). Similar to the $\text{UO}_2^{2+}/\text{Br}^-$ solution, the spectrum of the $\text{UO}_2^{2+}/\text{I}^-$ solution exhibited the broad $\text{UO}_2^+(\text{V})$ signal ($g=2.08$), indicating that $\text{UO}_2^{2+}(\text{VI})$ [in the form of $\text{U}^{\text{VI}}\text{O}_2(\text{H}_2\text{O})_n^{2+}$, $n = 3-5$] had been reduced to $\text{UO}_2^+(\text{V})$ [in the form of $\text{U}^{\text{V}}\text{O}_2(\text{H}_2\text{O})_n^+$, $n = 3-5$] thermally by I^- via the charge-transfer of iodide to uranyl(VI) (Equation 1). Presumably, I^- was simultaneously oxidized to $\text{I}^\bullet$ which subsequently combined with I^- in the medium to give the iodide-iodine ion-radical pair ($\text{I}_2^{\bullet-}$). Simultaneously, some $\text{I}^\bullet$ radicals combined to form I_2 . Formation of I_2 in the reaction was confirmed by a starch test by the treatment of the solution with starch giving a dark blue color immediately.

The possible formation of $\text{X}_2^{\bullet-}$ in the $\text{UO}_2^{2+}/\text{X}^-$ ($\text{X} = \text{Br}$ or I) aqueous system upon laser flash photolysis was suggested earlier by Burrows [22] based on the electronic spectroscopic data on the photochemical reaction. However, $\text{UO}_2^+(\text{V})$ was not identified from the reaction. In this work, we have provided by EPR spectroscopy direct evidence for formation of $\text{UO}_2^+(\text{V})$ [in the form of $\text{U}^{\text{V}}\text{O}_2(\text{H}_2\text{O})_n^+$, $n = 3-5$] through a thermal chemical redox reaction of X^- ($\text{X} = \text{Br}$ or I) and $\text{UO}_2^{2+}(\text{VI})$ [in the form of $\text{U}^{\text{VI}}\text{O}_2(\text{H}_2\text{O})_n^{2+}$, $n = 3-5$]. As some bromine or iodine radicals produced from the redox reaction combined with the halide anion reversibly to form stable $\text{X}_2^{\bullet-}$ anion-radical pairs ($\text{X} = \text{Br}$ or I), many other halogen radicals associated each other favorably to give the X_2 molecules (reddish brown for Br_2 and brown for I_2 as seen in the reaction solutions). The overall chemical process in the $\text{UO}_2^{2+}/\text{X}^-$ system is shown below

(X = Br or I)

The tetracoordinated $\text{UO}_2\text{Br}_4^{2-}$ anion by bromide that contains stable U(VI)–Br bonds in the equatorial positions of $\text{UO}_2^{2+}(\text{VI})$ has been synthesized previously by reaction of UO_2^{2+} (1 m) with concentrated aqueous HBr (11 m) [9]. At lower acidity and concentrations of UO_2^{2+} and Br[−] as was the case in this work, the U(VI)–Br bond was not formed. Instead, $\text{UO}_2^{2+}(\text{VI})$ was effectively reduced to $\text{UO}_2^+(\text{V})$ by bromide through the intermolecular charge-transfer as described in Equation 1.

3.3 Charge-transfer absorption of Uranyl(VI)–DMSO and Related Chemical Oxidation-reduction

Dimethyl sulfoxide (DMSO) is a very common, major aprotic organic solvent. In this work, we have studied behavior of uranyl in this non-aqueous solvent. The solubility of uranyl(VI) nitrate (source of UO_2^{2+} used throughout this work) in the neat DMSO is very small. After introducing concentrated sulfuric acid (98%) to DMSO forming homogeneous mixtures, we were able to dissolve uranyl(VI) nitrate in the DMSO– H_2SO_4 mixtures to a certain extent to make homogeneous solutions of UO_2^{2+} at 0.050 M. Figure 7 shows the UV-visible spectra of UO_2^{2+} (0.050 M) in the different DMSO– H_2SO_4 mixtures with molar concentrations of H_2SO_4 being 2.0 M, 4.0 M, and 5.0 M, respectively. The spectrum (Figure 7a) of UO_2^{2+} in DMSO– H_2SO_4 (2.0 M) exhibited a characteristic π – π^* absorption band of the cation centered at 420 nm, together with appreciable charge-transfer absorption of UO_2^{2+} –DMSO at 350–400 nm. As the concentration of sulfuric acid in the DMSO– H_2SO_4 mixtures further increased to 4.0–5.0 M, the

intensity of the UO_2^{2+} –DMSO charge-transfer absorption at 350–400 nm was enhanced dramatically (Figure 7b with $[\text{H}_2\text{SO}_4] = 4.0 \text{ M}$, and Figure 7c with $[\text{H}_2\text{SO}_4] = 5.0 \text{ M}$), and the UO_2^{2+} π – π^* absorption band centered at 420 nm was mostly blurred. All this is comparable to the situation for the uranyl-bromide charge-transfer absorption as described above in Figure 3. The observed UO_2^{2+} –DMSO charge-transfer absorption is reasonably resulted from the single-electron transfer from the protonated DMSO to the valence shell of uranium in $\text{UO}_2^{2+}(\text{VI})$. It implies that an oxidation-reduction reaction may take place between $\text{UO}_2^{2+}(\text{VI})$ and DMSO in the presence of sulfuric acid.

A solution of UO_2^{2+} (0.050 M) in DMSO– H_2SO_4 (2.0 M) was made and kept in the dark at ambient temperature for 24 h, and it was then characterized by EPR spectroscopy at 80 K. The EPR spectrum (Figure 8) showed a broad signal of $\text{UO}_2^+(\text{V})$ with $g=2.07$. In addition, a sharp signal (singlet) with $g=2.01$ was observed. It is attributable to the $\text{DMSO}^\bullet$ ($\text{CH}_3\text{SOCH}_2^\bullet$) radical by referencing to a previous study [25]. Opstad et.al. found from their study [25] that CH_3SOCH_3 (DMSO) was readily oxidized to the long-lived $\text{CH}_3\text{SOCH}_2^\bullet$ ($\text{DMSO}^\bullet$) radical via a C–H bond abstraction by an alkoxide base (RO^-) present in the solvent. The stabilization of the radical was achieved by delocalization of the radical center within the solvent host via formation of a radical–solvent (DMSO – $\text{DMSO}^\bullet$) pair (cf. the above-mentioned anion-radical pair $\text{Br}_2^{\bullet-}$), which allowed characterization of the radical by EPR spectroscopy [25]. In this work, we have demonstrated an alternative approach to generating the stable $\text{CH}_3\text{SOCH}_2^\bullet$ radical by oxidation of CH_3SOCH_3 with $\text{UO}_2^{2+}(\text{VI})$ in the presence of sulfuric acid. This oxidation-reduction is believed to take place through the uranyl(VI)–DMSO charge-transfer pathway as shown below (Equation 2).

The increase in intensity of charge-transfer absorption by acid as demonstrated by Figure 7 is reasonably related to protonation on the sulfoxide oxygen ($\text{S}=\text{OH}^+$) in DMSO by the existing sulfuric acid. The protonation enhances the acidity of the C–H bond in DMSO (cf. protonation of acetone), making the bonding electrons more active (reductive) that is believed to lead to stronger charge-transfer absorption. Therefore, most likely, in the presence of a strong acid it is a C–H electron that is transferred to the uranium valence shell in $\text{UO}_2^{2+}(\text{VI})$ to reduce it to $\text{UO}_2^+(\text{V})$ and to effect the charge-transfer absorption (Equation 2). Electron-transfer from oxygen or sulfur to $\text{UO}_2^{2+}(\text{VI})$ would be unfavorable because of the positive charge introduced to the sulfoxide ($\text{S}=\text{O}$) group by protonation.

3.4 Charge-transfer Oxidation-reduction of Uranyl(VI) and Phenol

Phenol (PhOH or $\text{C}_6\text{H}_5\text{OH}$) is an effective and efficient organic reducing agent. In this work, we have studied oxidation-reduction reaction of phenol and uranyl(VI) in the acetone media. In liquid acetone $\text{UO}_2^{2+}(\text{VI})$ has been shown to be coordinated by five acetone molecules in the equatorial positions of the central uranium via the $(\text{CH}_3)_2\text{CO}:\rightarrow\text{UO}_2^{2+}$ bonds [14]. The $\text{UO}_2^{2+}(0.02\text{--}0.10\text{M})\text{--PhOH}(0.05\text{--}0.5\text{M})$ mixtures in acetone exhibited characteristic charge-transfer absorption of $\text{UO}_2^{2+}(\text{VI})$ [in the form of $\text{U}^{\text{VI}}\text{O}_2(\text{acetone})_5^{2+}$] at 350–400 nm (Figure 9), with the structure of their UV-visible spectra comparable to that of the above-described charge-transfer absorption spectra of $\text{UO}_2^{2+}/\text{Br}^-$, $\text{UO}_2^{2+}/\text{I}^-$, and $\text{UO}_2^{2+}/\text{DMSO}$ systems. This is also consistent with the charge-transfer absorption between UO_2^{2+} and 4-chlorophenol ($p\text{-ClC}_6\text{H}_4\text{OH}$)

as previously reported by Sarakha et.al. [23]. Similar to the $\text{UO}_2^{2+}/\text{Br}^-$ and $\text{UO}_2^{2+}/\text{I}^-$ charge-transfer absorptions, we have found (Figure 9) that the intensity (A_{375} , absorbance at 375 nm) of the charge-transfer absorption of $\text{UO}_2^{2+}/\text{PhOH}$ is directly proportional to the molar concentrations of UO_2^{2+} and PhOH , respectively, showing the nature of bimolecular interaction between UO_2^{2+} and PhOH in the charge-transfer absorption transition [a single-electron transfer from phenol to uranyl(VI)].

A mixture of UO_2^{2+} (0.10M) and PhOH (0.50 M) in acetone was prepared and the reaction was allowed to proceed at room temperature for different times (0 day, 1 day, and 3 days). The UV-visible spectra of the mixture were then recorded (Figure 10). Figure 10 shows that the absorption of the reaction mixture in 350-400 nm increased over time, attributable to formation of the phenoxyl $\text{PhO}^\bullet$ radical [26]. Likely, the reaction was completed in 1-3 days on the basis of the change in the spectra.

An acetone solution containing UO_2^{2+} (0.10 M) and PhOH (0.50 M) was characterized by EPR spectroscopy (24 h after the solution was prepared). The EPR spectrum (80 K, Figure 11a) exhibited a broad signal of $\text{UO}_2^+(\text{V})$ [presumably in the form of $\text{U}^{\text{V}}\text{O}_2(\text{acetone})_5^+$] with $g=2.08$ and a sharp singlet signal with $g=2.00$, attributable to the phenoxyl $\text{PhO}^\bullet$ radical [27]. We also recorded the EPR spectrum of the UO_2^{2+} (0.050 M)– PhOH (0.50 M) solution in acetone. The spectrum at 80 K exhibited the strong signals of $\text{UO}_2^+(\text{V})$ and $\text{PhO}^\bullet$, essentially the same as those in Figure 11a. The EPR spectrum of the UO_2^{2+} (0.010 M)– PhOH (0.050 M)–acetone solution (with lower concentrations of uranyl and phenol) showed the broad $\text{UO}_2^+(\text{V})$ signal and very weak $\text{PhO}^\bullet$ signal. In the presence of sulfuric acid, the EPR spectrum (80 K, Figure 11b) of the UO_2^{2+} (0.10 M)– PhOH (0.50 M)– H_2SO_4 (2 M)–acetone solution exhibited very strong $\text{PhO}^\bullet$ signal,

but the $\text{UO}_2^+(\text{V})$ signal (very weak) mostly disappeared presumably due to disproportionation of uranium(V) to uranium(VI) and uranium(IV). All the EPR data demonstrated that an oxidation–reduction reaction of $\text{UO}_2^{2+}(\text{VI})$ [in the form of $\text{U}^{\text{VI}}\text{O}_2(\text{acetone})_5^{2+}$] and PhOH had happened via the following charge-transfer pathway (Equation 3), giving $\text{UO}_2^+(\text{V})$ [in the form of $\text{U}^{\text{V}}\text{O}_2(\text{acetone})_5^+$] and a stable, long-lived phenoxyl $\text{PhO}^\bullet$ radical in the acetone media.

Zubarev et.al. showed by EPR studies that at liquid nitrogen temperature (77 K) the highly unstable 2,6-di-*tert*-butyl-4-methylphenol radical cation ($\text{ArOH}^{+\bullet}$) was produced on γ -irradiation of the phenol (ArOH) in the alkyl halide matrix, and then $\text{ArOH}^{+\bullet}$ underwent subsequent rapid deprotonation upon warming up above 107 K to the more stable phenoxyl radical ($\text{ArO}^\bullet$) [27]. Since our reaction was conducted at ambient temperature, most likely, the single-electron transfer (charge-transfer) and deprotonation described in Equation 3 took place simultaneously, without forming a highly unstable intermediate phenol radical cation $\text{PhOH}^{+\bullet}$. Photolytic studies performed by Sarakha et.al. [23] have shown that 4-chlorophenol (*p*- $\text{ClC}_6\text{H}_4\text{OH}$) undergoes photochemical oxidation by the excited state of $\text{UO}_2^{2+}(\text{VI})$. But no reaction between 4-chlorophenol and uranyl(VI) in the ground state (in the dark) was found. In this work, we have identified thermal chemical oxidation of phenol (more reductive than 4-chlorophenol) by uranyl(VI) by an EPR spectroscopic study. The reaction reasonably followed the simultaneous charge-transfer and deprotonation pathway as described in Equation 3. A related stable 2,4,6-tri-*tert*-butylphenoxyl radical ($2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O}^\bullet$) has been isolated in the

solid state and structurally characterized [28]. The structural data and theoretical calculations indicated substantive delocalization of the single electron to the *ortho*- and *para*-carbons stabilizing the radical. By comparison, we believe that delocalization of the single electron to the phenyl ring for PhO[•] also occurs, making PhO[•] long-lived in acetone at ambient temperature.

4. Conclusions

The charge-transfer absorption transition of uranyl UO₂²⁺(VI) (hydrated) in the aqueous halide(Br⁻ or I⁻) solution has been identified at 350-400 nm from UV-visible spectroscopic studies. It originates from a single-electron transfer from a halide anion to the uranium(VI) valence shell. The intensity of the charge-transfer absorption (represented by absorbance at 375 nm) has been found directly proportional to molar concentrations of both halide (Br⁻ or I⁻) and uranyl(VI), showing the nature of bimolecular interaction between halide and uranyl(VI) in the charge-transfer absorption transition. In the presence of sulfuric acid, the absorbance at 375 nm (charge-transfer absorption) of the UO₂²⁺(VI)–halide solution has also been shown to be directly proportional to molar concentration of the acid most likely because a strong acid facilitates more Br⁻ anions to contact the uranium center, enhancing the charge-transfer transition. The charge-transfer absorption of uranyl UO₂²⁺(VI) in the DMSO solution in the presence of sulfuric acid has been found from a UV-visible spectroscopic study. Its intensity increases as the concentration of the acid is getting greater. Thus, the absorption most likely originates from the single-electron transfer from protonated DMSO to uranyl(VI).

Studies of photochemical and electrolytic reduction of uranyl(VI) to uranyl(V) have been reported previously [20-23,29,30]. In this work, we have investigated thermal chemical reduction of uranyl(VI) (diamagnetic) to uranyl(V) (paramagnetic) with bromide, iodide, DMSO, and

phenol by EPR spectroscopy. The outcomes serve as further evidence to support the charge-transfer transition between uranyl(VI) and each of the reductants. An alternative method of generating the DMSO[•] radical [25,31] by oxidation-reduction reaction of DMSO with UO₂²⁺ in the presence of sulfuric acid was developed, and the possible mechanism has been proposed. The thermal chemical oxidation-reduction reaction of UO₂²⁺(VI) [in the form of U^{VI}O₂(acetone)₅²⁺] and PhOH in acetone takes place to give UO₂⁺(V) [in the form of U^{VI}O₂(acetone)₅²⁺] and PhO[•] via a simultaneous charge-transfer and deprotonation pathway.

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6. References

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Figures

Figure 1

(a) The UV-visible spectra of UO_2^{2+} (0.10 M) in the NaBr (aq) solutions. From bottom to top, $[\text{NaBr}] = 0$ M (pure water, #1), 1.2 M (#2), 2.0 M (#3), 2.8 M (#4), 3.6 M (#5), 4.5 M (#6), 5.3 M (#7), and 6.0 M (#8). Plot of A_{375} (absorbance at 375 nm) versus $[\text{NaBr}]$ (molar concentration of NaBr) shows a linear relationship, with $A_{375} = 0.391[\text{NaBr}] + 0.257$ ($R^2 = 0.96$); and (b) The UV-visible spectra of UO_2^{2+} (0.10 M) in the KI (aq) solutions. From bottom to top, $[\text{KI}] = 0$ M (pure water, #1), 0.10 M (#2), 0.50 M (#3), and 0.80 M (#4). Plot of A_{375} versus $[\text{KI}]$ (molarity) shows a linear relationship, with $A_{375} = 1.79[\text{KI}] + 0.38$ ($R^2 = 0.99$).

Figure 2

(a) The UV-visible spectra of UO_2^{2+} [0 M (#1), 0.020 M (#2), 0.040 M (#3), 0.060 M (#4), 0.080 M (#5), and 0.10 M (#6)] in the aqueous media containing 4.0 M NaBr. Plot of A_{375} (absorbance at 375 nm) versus $[\text{UO}_2^{2+}]$ (molar concentration of UO_2^{2+}) shows a linear relationship, with $A_{375} = 15.67[\text{UO}_2^{2+}] + 0.058$ ($R^2=0.998$); and (b) The UV-visible spectra of UO_2^{2+} [0 M (#1), 0.020 M (#2), 0.040 M (#3), 0.060 M (#4), and 0.10 M (#5)] in the aqueous media containing 0.50 M KI. Plot of A_{375} versus $[\text{UO}_2^{2+}]$ shows a linear relationship, with $A_{375} = 8.07[\text{UO}_2^{2+}] + 0.15$ ($R^2=0.98$).

Figure 3

The UV-visible spectra of UO_2^{2+} (0.10 M) in the aqueous media containing 3.0 M NaBr and different concentrations of sulfuric acid. From bottom to top, $[\text{H}_2\text{SO}_4]$ = 0.5 M (#1), 1.0 M (#2), 2.0 M (#3), 2.5 M (#4), and 3.0 M (#5). Plot of A_{375} (absorbance at 375 nm) versus $[\text{H}_2\text{SO}_4]$ (molar concentration) shows a linear relationship, with $A_{375} = 0.439[\text{H}_2\text{SO}_4] + 0.683$ ($R^2=0.96$).

Figure 4

(a) The UV-visible spectra of UO_2^{2+} (0.10 M) in the neutral 4.5 M NaBr(aq) aqueous solution at different times [0 h (red line, bottom), 18 h (green line, middle), and 47 h (black line, top)] after the solution was made; (b) The UV-visible spectra of an aqueous mixture of UO_2^{2+} (0.10 M)-NaBr(4.5 M)- H_2SO_4 (2M) at different times [0 h (blue line, bottom) and 9 h (red line, top)] after the mixture was made.

Figure 5

The EPR spectrum (80 K) of uranyl $\text{UO}_2^+(\text{V})$ (hydrated) ($g=2.08$) generated in the aqueous solution of $\text{UO}_2^{2+}(\text{VI})$ (0.10 M)–NaBr(4.5 M)– H_2SO_4 (2 M) (24 h after the solution was made).

Figure 6

(a) The UV-visible spectra of a mixture of UO_2^{2+} (0.10M) and KI (0.50 M) in neutral aqueous solution recorded at different times (0 h, 1 h, 18 h, and 26 h from bottom to top) after the mixture was prepared; and (b) The EPR spectrum (80 K) of uranyl $\text{UO}_2^+(\text{V})$ (hydrated) ($g=2.08$) generated in the neutral aqueous solution of $\text{UO}_2^{2+}(\text{VI})$ (0.10 M)–KI(1 M) (24 h after the solution was made).

Figure 7

The UV-visible spectra of UO_2^{2+} (0.05 M) in DMSO in the presence of sulfuric acid at different concentrations. (a) $[\text{H}_2\text{SO}_4] = 2.0 \text{ M}$, (b) $[\text{H}_2\text{SO}_4] = 4.0 \text{ M}$, and (c) $[\text{H}_2\text{SO}_4] = 5.0 \text{ M}$.

Figure 8

The EPR spectrum (80 K) of uranyl $\text{UO}_2^+(\text{V})$ ($g=2.07$) and $\text{CH}_3\text{SOCH}_2\cdot$ ($\text{DMSO}\cdot$) radical ($g=2.01$) generated in the CH_3SOCH_3 (DMSO) solution of $\text{UO}_2^{2+}(\text{VI})$ (0.05 M) in the presence of sulfuric acid (2 M) (with a tilted baseline possibly due to inhomogeneity of the sample at liquid nitrogen temperature).

Figure 9

(a) The UV-visible spectra of UO_2^{2+} (0.050 M) in the acetone solutions containing PhOH at different concentrations. From bottom to top, [PhOH] = 0 M, 0.050 M, 0.10 M, 0.15 M, 0.20 M, 0.25 M, and 0.30 M. Plot of A_{375} (absorbance at 375 nm) versus [PhOH] (molarity) shows a linear relationship, with $A_{375} = 1.52[\text{PhOH}] + 0.30$ ($R^2=0.97$); and (b) The UV-visible spectra of UO_2^{2+} in the acetone solutions containing 0.05 M PhOH. From bottom to top, $[\text{UO}_2^{2+}] = 0$ M, 0.020 M, 0.040 M, 0.060 M, 0.080 M, and 0.10 M. Plot of A_{375} versus $[\text{UO}_2^{2+}]$ shows a linear relationship, with $A_{375} = 4.95[\text{UO}_2^{2+}] + 0.11$ ($R^2=0.96$).

Figure 10

The UV-visible spectra of a mixture of UO_2^{2+} (0.10M) and PhOH (0.50 M) in acetone recorded at different times [0 day (black line, bottom), 1 day (red line, middle), and 3 days (blue line, top)] after the mixture was prepared.

Figure 11

The EPR spectra (80 K) of uranyl $\text{UO}_2^+(\text{V})$ [in the form of $\text{U}^{\text{V}}\text{O}_2(\text{acetone})_5^+$] ($g=2.08$) and phenoxyl ($\text{PhO}^\cdot$) radical ($g=2.00$) generated from (a) the $\text{UO}_2^{2+}(\text{VI})(0.10 \text{ M})$ – $\text{PhOH}(0.50 \text{ M})$ –acetone solution, and (b) the $\text{UO}_2^{2+}(\text{VI})(0.10 \text{ M})$ – $\text{PhOH}(0.50 \text{ M})$ – $\text{H}_2\text{SO}_4(2 \text{ M})$ –acetone solution 24 h after the solutions were prepared.

GRAPHICAL ABSTRACT