# Photochemistry of Uranyl(VI) Tributylphosphate in Supercritical $CO_2$: An Evidence of Photochemical Reduction by Ethanol

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The photochemistry of uranyl(VI)-tributylphosphate (TBP) complex in supercritical carbon dioxide ($scCO_2$) was studied in the pressure range of 8-40 MPa and from 289 to 336 K. Deactivation rate constants decreased with the increase of pressure. Temperature dependence analysis of the deactivation rate constants indicated that $scCO_2$ contributes differently to deactivation processes from liquid phase $CO_2$ based on activation barriers. An UV irradiation experiment proved photochemical reduction of uranyl(VI)-TBP complex by ethanol in $scCO_2$.

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Supercritical carbon dioxide ($scCO_2$) is an environmentally friendly solvent whose nature can be widely variable by temperature and pressure.[1] Its application for the extraction of metallic species from liquid or even solid matrices has been earned great interest recently. UV-visible and emission spectroscopic methods have been proven to be useful for monitoring the behaviour of solutes in supercritical fluids (SCFs).[2-4] However, little information is available about spectroscopy and photochemistry of uranyl(VI) complexes in SCFs.[5,6] No investigation has been conducted on the photoreduction of uranyl(VI) compounds in spite the well known reactivity of excited uranyl(VI), and such reaction can find application in nuclear fuel reprocessing. Moreover, fundamental data about solvation mechanisms (such as local density augmentation and preferential solvation, which are characteristic phenomena of SCFs) can be obtained.[2-4]

The measurements were carried out using a high-pressure and high-temperature cell (Taiatsu Glass Co., Ltd.) with three sapphire windows for absorption and emission measurements. The temperature was monitored by a thermocouple recessing inside the middle of the cell and controlled with electric heating rods inserted into the cell body. The pressure was controlled with an Isco MODEL 260D syringe pump. Absorption spectra were measured on a Shimadzu UV-2400PC spectrophotometer. Emission decay curve measurements were carried out using a Horiba NAES-500 nanosecond fluorimeter with nitrogen laser excitation at 337.1 nm. Uranyl(VI) tributylphosphate complex was prepared by dissolving uranyl(VI) nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, in tributylphosphate (TBP; Acros Organics, 99%). The uranyl concentration of this stock solution was 0.1 mol $dm^{-3}$ with about 36-fold excess of TBP. After flushing the cell with a slow stream of $CO_2$, a known amount of the stock solution was introduced with a micro syringe and the cell was closed. After the pressure was increased, the cell was overturned several times to obtain a homogeneous solution. For the observation of photochemical reaction, tenfold excess of ethanol (over uranyl) was added to the solution. A high-pressure mercury lamp (USH-500D, Ushio) was used for irradiation, its most intense lines at 436, 405, and 365 nm match the excitation of the uranyl complex.

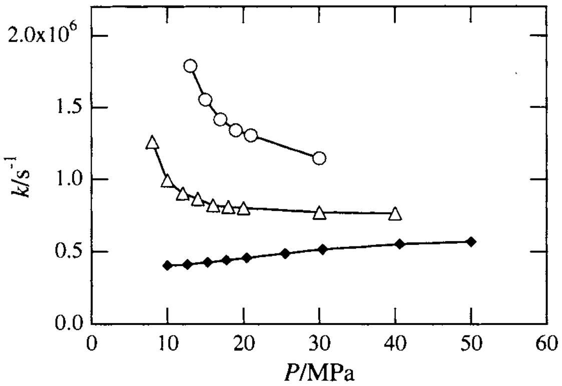

**Figure 1.** Pressure dependence of the deactivation rate constant of uranyl-TBP complex at 308 K (△) and 333 K (○). Concentration of uranyl(VI) nitrate and TBP in the $scCO_2$ solution was $8x10^{-3}$ mol $dm^{-3}$ and 0.3 mol $dm^{-3}$, respectively. Literature data[6] is also included for comparison (◆).

All of the emission decay traces obtained were analyzed as single exponential functions, which ensures a single emissive species in the solvent. The deactivation rate constants ($k$), which are the sum of the radiative ($k^r$) and nonradiative ($k^{nr}$) rate constants as $k = k^r + k^{nr}$, are determined for uranyl(VI) tributylphosphate complex in $scCO_2$ under various pressures at 308 K and 333 K (Figure 1). Since the observed radiative rate constants are known to proportional to (i) the square of the refractive index of the medium[7,8] and (ii) the cube of the emission energy of the uranyl(VI) complexes,[9] the changes in the radiative rate constants are negligible due to the values of $k^r$ are about 3 orders smaller than $k^{nr}$.[9] Thus the variation in $k$ can be analyzed in terms of $k^{nr}$.

The literature data of Addleman *et al.* [6] is also included in Figure 1. It is worthwhile to note that in the high pressure region all the data seem to converge to *ca.* $8x10^5$ $s^{-1}$. The difference with the data of Addleman *et al.* may be attributed to the less concentration (μmolar level) of TBP in the $scCO_2$ solution. Due to its high concentration TBP may be considered as a cosolvent in our experiments.

It is well documented in the literature[2-4] that in low density SCF - cosolvent systems preferential solvation of the solute by the cosolvent may occur. At low pressure when the SCF ($CO_2$) is in a low-density gaslike state, the local environment around the solute (uranyl TBP complex) is enriched by the cosolvent (TBP). The enhanced TBP concentration in its

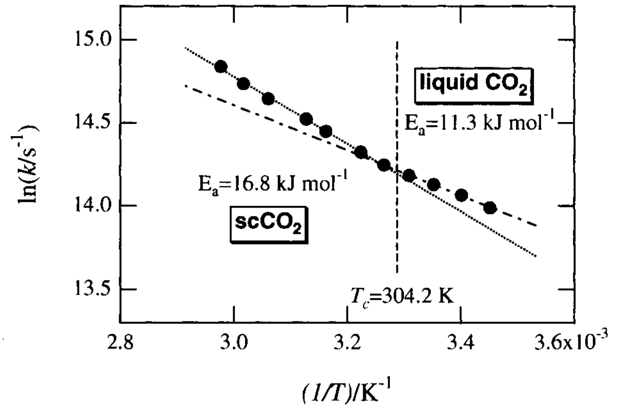

**Figure 2.** Arrhenius plot for the deactivation rate constants of uranyl tributylphosphate complex in $CO_2$. The pressure was constant to 20 MPa. Concentration of uranyl(VI) nitrate and TBP in the $scCO_2$ solution was $8\times10^{-3}$ mol dm$^{-3}$ and 0.3 mol dm$^{-3}$, respectively.

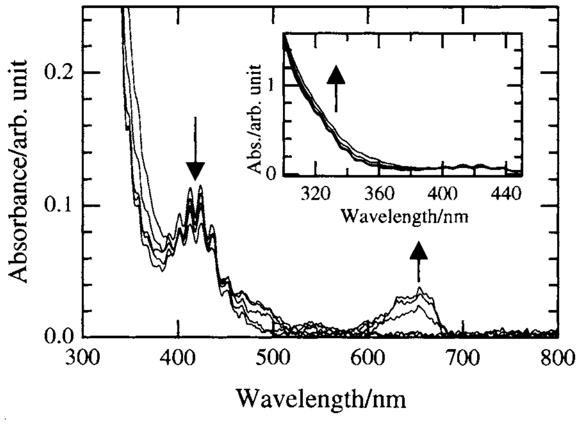

**Figure 3.** Changes in absorption spectra of uranyl(VI) tributylphosphate complex solution in $scCO_2$ at 333 K and 20 MPa when irradiated by a high pressure mercury lamp. Spectra were observed at 0, 15, 30, 65 and 110 min from the starting of the irradiation. Concentration of uranyl(VI) nitrate, TBP and ethanol in the $scCO_2$ solution was $1.7\times10^{-2}$ mol dm$^{-3}$, 0.6 mol dm$^{-3}$ and 0.19 mol dm$^{-3}$, respectively.

proximity contributes to the nonradiative deactivation of the excited uranyl ion. With the increase of pressure, the density of $scCO_2$ increases, and it replaces the TBP molecules in the solvation shell of the complex, leading to similar lifetimes like in conventional solvents.

Figure 2 shows the temperature dependence of the deactivation rate constants determined at 20 MPa (Figure 2). For the above and below the critical temperature ($T_c$ =304.2 K) of $CO_2$ the distinct difference of the activation energy was calculated as $E_a$= 16.8 kJ mol$^{-1}$ ($T > T_c$) and $E_a$= 11.3 kJ mol$^{-1}$ ($T < T_c$). The difference in the activation energy below and above the critical transition requires further investigations which are in progress, but certainly it should be attributed to the difference of the mode of the nonradiative deactivation.

Ethanol is known as a strong reductive quencher to the excited uranyl(VI) ion.[10] The quenching rate constant of ethanol against the excited uranyl(VI)-TBP complex should be very small. The examination of the Stern-Volmer relationship was not possible because the deactivation rate constants determined for the solution including ethanol up to 0.2% were almost identical to the solution without ethanol, and the addition of more ethanol turns the system into a three-component mixed solvent. However, the absorption spectra of irradiated uranyl(VI)-TBP complex in $scCO_2$ with ethanol gave a clear evidence of photochemical reduction. With time of exposure to light up to 110 min, the decrease in absorbance of spectra of uranyl(VI) tributylphosphate at *ca.* 420 nm was observed (Figure 3). Simultaneously, the growth of absorption bands were also observed at around 680 nm and at the UV region below 360 nm which corresponds to uranium(IV) and uranium(V),[11,12] respectively. No photoreaction between TBP and the excited uranyl ion was reported so far, therefore we can conclude that ethanol acted as a reducing agent, as such reaction of alcohols is well known in uranyl photochemistry.[10] Since no direct reduction of uranyl(VI) to uranium(IV) was reported, this result may be interpreted as that the uranyl(VI) complex was reduced to uranium(V) by irradiation and the uranium(IV) was produced by the disproportionation reaction from the resultant uranium(V). The disproportionation reaction of uranium(V) requires 4-fold protons which can be supplied by the crystal water of uranyl(VI) nitrate hexahydrate or by the ethanol. It is prominent to note that the broad band of uranium(V) can be observed in this steady state method probably due to the stability of the uranium(V) species in $scCO_2$. This photochemical reaction and the remarkable stability of uranium(V) in $scCO_2$ medium require further detailed investigations.

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## References and Notes

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