

# Photoreduction of uranyl ion in aqueous solution. I. With ethanol in sulphuric acid solutions

Ryuji Nagaishi<sup>a</sup>, Yosuke Katsumura<sup>a,\*</sup>, Kenkichi Ishigure<sup>a</sup>, Hisao Aoyagi<sup>b</sup>, Zenko Yoshida<sup>b</sup>,  
Takaumi Kimura<sup>b</sup>

<sup>a</sup> Department of Quantum Engineering and Systems Science, Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

<sup>b</sup> Japan Atomic Energy Research Institute, Tokai, Naka-gun, Ibaraki 319-11, Japan

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## Abstract

Photoreduction of  $\text{UO}_2^{2+}$  with ethanol (EtOH) in  $\text{H}_2\text{SO}_4$  solutions has been studied by an electrochemical quantitative analysis of  $\text{U}^{\text{IV}}$  formed as a final product. The quantum yield  $\phi(\text{U}^{\text{IV}})$  of  $\text{U}^{\text{IV}}$  increased rapidly at  $[\text{EtOH}]$  up to  $0.5 \text{ mol dm}^{-3}$  and then reached a maximum under deaerated  $3.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . At  $[\text{EtOH}] = 1.5 \text{ mol dm}^{-3}$ ,  $\phi(\text{U}^{\text{IV}})$  under deaerated conditions increased gradually with  $[\text{H}_2\text{SO}_4]$ , while  $\phi(\text{U}^{\text{IV}})$  under oxygenated conditions was almost one-half of that under deaerated conditions.

In order to explain these experimental results,  $\phi(\text{U}^{\text{IV}})$  was expressed on the basis of both formation of an encounter complex between excited  $\text{UO}_2^{2+}$  ( $^*\text{UO}_2^{2+}$ ) and EtOH and a successive reaction of  $\text{UO}_2^{2+}$  with  $\alpha$ -hydroxyalkyl radical formed after the complex formed.

Kinetic parameters for the quenching of  $^*\text{UO}_2^{2+}$  by EtOH were derived from a plot of  $\phi(\text{U}^{\text{IV}})^{-1}$  vs.  $[\text{EtOH}]^{-1}$  and checked by the measurements of the photon emission from  $^*\text{UO}_2^{2+}$  with a time-resolved laser and steady state light excitation. It was confirmed that the proposed photoreduction mechanism could reproduce the experimental results.

**Keywords:** Uranyl ion; Sulphuric acid; Ethanol; Photoreduction; Photoemission; Quenching

## 1. Introduction

The photochemistry of uranyl ion ( $\text{UO}_2^{2+}$ ) in aqueous solutions has been investigated to a considerable extent, and review articles exist [1,2]. It is well known that  $\text{UO}_2^{2+}$  has a visible absorption band below 500 nm and that uranyl ion in the lowest excited state ( $^*\text{UO}_2^{2+}$ ) emits photons in the wavelength range 460–600 nm and can be easily photoreduced into  $\text{U}^{\text{IV}}$  in the presence of suitable organic compounds, such as alcohols.

Concerning the photoreduction, a lot of research [3–16] has been carried out from the viewpoint of the valence conditioning of uranium ions in analytical chemistry [3,4] and spent nuclear fuel reprocessing [5–8]. It is a multistep process from the deactivation of  $^*\text{UO}_2^{2+}$  to chemical reactions of uranium ions. The quenching of  $^*\text{UO}_2^{2+}$  by additives in the deactivation has been measured from its lifetime and spectrum [13–16]. The quantum yields  $\phi(\text{U}^{\text{IV}})$  of resultant  $\text{U}^{\text{IV}}$

under various conditions [3–16] have been obtained. However, since few systematic studies have been carried out on the effects of the concentrations of solvent and solute and of dissolved  $\text{O}_2$  on  $\phi(\text{U}^{\text{IV}})$  and the quenching of  $^*\text{UO}_2^{2+}$ , the photoreduction mechanism is still not clear.

In the present experiment a systematic study of the photoreduction was carried out in sulphuric acid ( $\text{H}_2\text{SO}_4$ )–ethanol (EtOH) system, where a lot of research has been reported because EtOH is well known as one of the most reactive organic reducing agents and no byproduct resulted from sulphate ion. The quantum yield  $\phi(\text{U}^{\text{IV}})$  was determined by absolute measurements based on the electrochemical oxidation of  $\text{U}^{\text{IV}}$  to  $\text{UO}_2^{2+}$ , instead of the commonly used photoabsorption of  $\text{U}^{\text{IV}}$  at 650 nm. The lifetime and quenching of photoemission from  $^*\text{UO}_2^{2+}$  were measured by use of steady state or time-resolved exciting light. The photoreduction of  $\text{UO}_2^{2+}$  with EtOH in  $\text{H}_2\text{SO}_4$  was studied on the basis of the effects of the concentrations of  $\text{H}_2\text{SO}_4$  and EtOH and of dissolved  $\text{O}_2$  on  $\phi(\text{U}^{\text{IV}})$  and the quenching of  $^*\text{UO}_2^{2+}$ .

\* Corresponding author. Tel. +81338122111 ext. 6979 Fax. +81358006858.

## 2. Experimental details

### 2.1. Chemicals

A stock solution of 0.5 mol uranyl sulphate  $\text{dm}^{-3}$  in 0.5 mol  $\text{H}_2\text{SO}_4$   $\text{dm}^{-3}$  was prepared from trioxouranium (JAERI-U2) and  $\text{H}_2\text{SO}_4$ . A specific sample was prepared by diluting the stock solution with double-distilled water and  $\text{H}_2\text{SO}_4$  and then adding EtOH. The concentration  $[\text{SO}_4^{2-}]$  of sulphate ion in the sample was adjusted by  $\text{H}_2\text{SO}_4$  and potassium sulphate. The sample was kept in the dark during and after addition of EtOH. Potassium ferrioxalate taken as an actinometer in photoreduction experiments was prepared according to Parker's procedure [17]. Chemicals used in this work were of reagent grade.

### 2.2. Photoreduction

Light from a 500 W mercury lamp (USH-500D, Ushio) was passed through an aqueous 10 vol.% copper sulphate solution and an interference filter (Asahi Spectra Co.) to select light ( $407 \pm 6$  nm), which was used as the exciting light for the photoreduction [16]. The light of wavelength  $407 \pm 6$  nm can be absorbed by  $\text{UO}_2^{2+}$  but not by  $\text{U}^{\text{IV}}$  in  $\text{H}_2\text{SO}_4$  solutions. The light was split by a quartz plate into two directions, and each was injected to the sample and the actinometer solution in quartz cells with a 5 cm path length. The intensity of the incident light for the sample was set at about 350 mW. The initial concentration of  $\text{UO}_2^{2+}$  in the sample was taken as 50  $\text{mmol dm}^{-3}$ . The actinometer was 20  $\text{mmol}$  ferrioxalate ion  $\text{dm}^{-3}$  in 50  $\text{mmol H}_2\text{SO}_4$   $\text{dm}^{-3}$  [17]. From the absorptions of the sample and actinometer solutions, the photons could be absorbed completely in each solution within the 5 cm path length. The number of photons absorbed in the sample was evaluated from that absorbed in the actinometer, which was evaluated from  $\phi(\text{Fe}^{2+}, 405 \text{ nm}) = 1.13$  [17].

The concentration of  $\text{U}^{\text{IV}}$  was measured by an electrochemical method involving flow coulometric analysis with column electrodes of glassy carbon fibres [18]. After irradiation with a constant interval (10–30 min), a small amount of the solution ( $40 \times 10^{-6}$ – $80 \times 10^{-6}$   $\text{dm}^3$ ) was sampled with a microsyringe and then injected into the flow coulometric system, and  $\text{U}^{\text{IV}}$  in the system quantitatively oxidized into  $\text{UO}_2^{2+}$ . On the basis of the quantity of electric charge  $Q$  (C) obtained in each measurement, the concentration  $c$  ( $\text{mol dm}^{-3}$ ) of  $\text{U}^{\text{IV}}$  could be determined from the following equation:

$$c = \frac{Q}{nFV}$$

where  $n = 2$  is the number of electrons involved in the oxidation of  $\text{U}^{\text{IV}}$  to  $\text{UO}_2^{2+}$ ,  $F$  is the Faraday constant (96 500 C  $\text{mol}^{-1}$ ), and  $V$  ( $\text{dm}^3$ ) is the sampling volume. The concentration of  $\text{Fe}^{2+}$  formed in the actinometer was determined in the same way.

Where not specified, all experiments were carried out under magnetic stirring and degassing of the sample by Ar or  $\text{N}_2$  gas at room temperature.

### 2.3. Photoemission from $^*\text{UO}_2^{2+}$

The decay of the photoemission from  $^*\text{UO}_2^{2+}$  was observed by spectrometric multichannel analysis (SMA) with a pulsed Nd:YAG laser ( $\lambda_{\text{ex}} = 266$  nm) [19]. The intensity, pulse width, and repetition of the laser were 1 mJ  $\text{pulse}^{-1}$ , 15 ns, and 10 Hz respectively. SMA data were a series of the emission spectrum of  $^*\text{UO}_2^{2+}$  taken at several time intervals after the pulse laser excitation, the time resolution of which was a little longer than that of the laser, i.e. 15 ns. The spectral resolution of the data was 0.5 nm. The emission spectra of  $^*\text{UO}_2^{2+}$  at various  $[\text{SO}_4^{2-}]$  and  $[\text{EtOH}]$  were obtained by a spectrofluorimeter (F-4500, Hitachi).

Since there were no differences in the photoemissions in the presence and absence of  $\text{O}_2$ , each sample in 1 cm  $\times$  1 cm quartz cells was irradiated without degassing.

## 3. Results and discussion

### 3.1. The yields of the photoreduction of $\text{UO}_2^{2+}$ with EtOH in $\text{H}_2\text{SO}_4$ solutions

The photoreduction of  $\text{UO}_2^{2+}$  with EtOH results in the formation of  $\text{U}^{\text{IV}}$  as a final product. The yield of the  $\text{U}^{\text{IV}}$  increased linearly with increasing number of photons absorbed in the solution as shown in Fig. 1(a). The quantum yield  $\phi(\text{U}^{\text{IV}})$  of  $\text{U}^{\text{IV}}$  corresponding to the slope of each plot was obtained by a least-squares linear fitting, where the maximum concentration of formed  $\text{U}^{\text{IV}}$  was set at less than 10% of the initial  $[\text{UO}_2^{2+}]$  to avoid secondary reactions. Several experiments were made at the same  $[\text{EtOH}]$ , leading to an experimental error in  $\phi(\text{U}^{\text{IV}})$  of less than 5%.

Fig. 1(a) shows that  $\phi(\text{U}^{\text{IV}})$  in deaerated 3.0 mol  $\text{H}_2\text{SO}_4$   $\text{dm}^{-3}$  solution increased from 0.27 at  $[\text{EtOH}] = 5$   $\text{mmol dm}^{-3}$  to 0.51 at 20  $\text{mmol dm}^{-3}$ . In order to understand the dependence in the wide range of  $[\text{EtOH}]$ ,  $\phi(\text{U}^{\text{IV}})$  was measured at  $[\text{EtOH}]$  from 2.5  $\text{mmol dm}^{-3}$  to 6.0  $\text{mol dm}^{-3}$  as shown in Fig. 1(b) for the deaerated 3.0 mol  $\text{H}_2\text{SO}_4$   $\text{dm}^{-3}$  solution.  $\phi(\text{U}^{\text{IV}})$  increased rapidly at  $[\text{EtOH}]$  up to 0.5 mol  $\text{dm}^{-3}$ , and then had a maximum (0.65) and slightly decreased at higher than 0.5 mol  $\text{dm}^{-3}$ , while  $\phi(\text{U}^{\text{IV}})$  reported by Bell and Buxton [5] slightly increased at higher  $[\text{EtOH}]$ . This suggests that at  $[\text{EtOH}]$  up to 0.5 mol  $\text{dm}^{-3}$  the quenching of  $^*\text{UO}_2^{2+}$  by EtOH forming  $\text{U}^{\text{IV}}$  competes with the other radiative and non-radiative deactivations and that at  $[\text{EtOH}]$  higher than 0.5 mol  $\text{dm}^{-3}$  the quenching becomes predominant among the deactivations.

In order to understand the effects of the concentrations of proton and sulphate ion on the photoreduction,  $\phi(\text{U}^{\text{IV}})$  against total  $[\text{SO}_4^{2-}]$  was measured as shown in Fig. 2. Irradiated samples were  $\text{H}_2\text{SO}_4$  and sulphate solutions containing

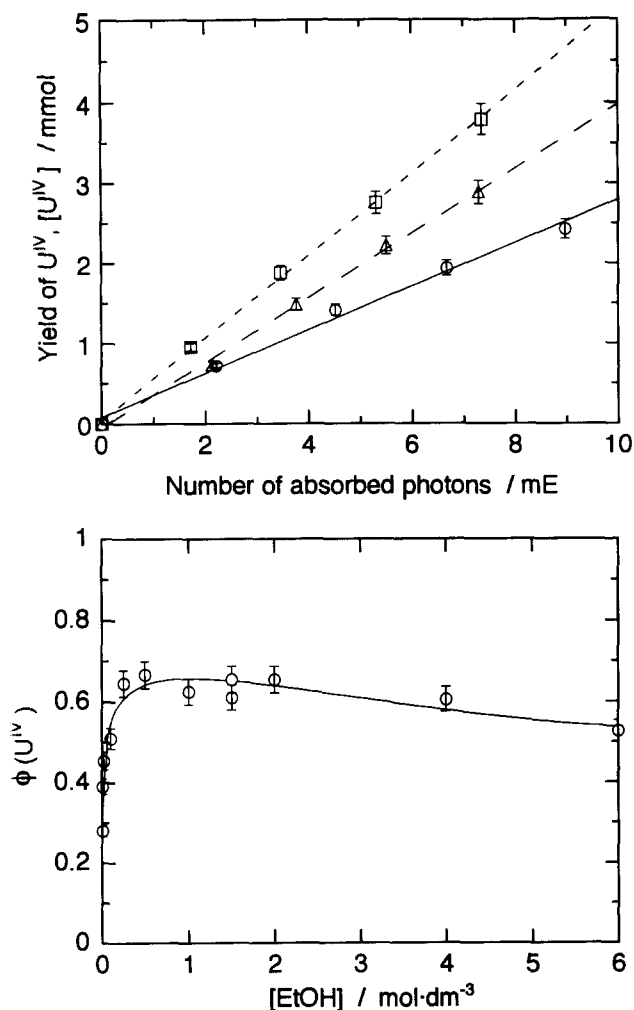


Fig. 1. The photoreduction of  $\text{UO}_2^{2+}$  with EtOH in  $3.0 \text{ mol H}_2\text{SO}_4 \text{ dm}^{-3}$ . a) Formation of  $U^{IV}$  as a function of number of absorbed photons:  $[\text{EtOH}] = 5 \text{ mol dm}^{-3}$  (○),  $10 \text{ mol dm}^{-3}$  (△), and  $20 \text{ mol dm}^{-3}$  (□). (b) Dependence of  $\phi(U^{IV})$  on  $[\text{EtOH}]$ . The solution was irradiated with  $407 \pm 6 \text{ nm}$  exciting light at  $20 \pm 2^\circ \text{C}$  under deaerated conditions. 1 einstein =  $6.022 \times 10^{23}$  photons).

$1.5 \text{ mol EtOH dm}^{-3}$ , in which the quenching of  $^*\text{UO}_2^{2+}$  by EtOH should be predominant among the deactivations as mentioned above.

In the deaerated  $\text{H}_2\text{SO}_4$  solutions,  $\phi(U^{IV})$  increased gradually with  $[\text{H}_2\text{SO}_4]$  from  $0.55$  ( $0.1 \text{ mol dm}^{-3}$ ) to  $0.80$  ( $8.0 \text{ mol dm}^{-3}$ ). The  $\phi(U^{IV})$  value of  $0.65$  at  $[\text{H}_2\text{SO}_4] = 3.0 \text{ mol dm}^{-3}$  agrees with  $0.58$ – $0.63$  reported by Bell and Buxton [5–7] and  $0.65$  by Kemp and Shand [11]. Bell and Buxton [5] also reported the dependence of  $\phi(U^{IV})$  in the  $[\text{H}_2\text{SO}_4]$  range up to  $3.0 \text{ mol dm}^{-3}$ , in which  $\phi(U^{IV})$  increased more rapidly with  $[\text{H}_2\text{SO}_4]$  than that in Fig. 2.

Included in Fig. 2 was  $\phi(U^{IV})$  in sulphate solutions which  $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$  and  $[\text{SO}_4^{2-}] = 0.5, 1.0, 1.5,$  and  $2.0 \text{ mol dm}^{-3}$ . Each  $\phi(U^{IV})$  in the sulphate solutions agreed well with that in  $\text{H}_2\text{SO}_4$  solutions at the same  $[\text{SO}_4^{2-}]$ . It was found that  $\phi(U^{IV})$  is mainly dependent on  $[\text{SO}_4^{2-}]$  but not on  $[\text{H}^+]$ .

In the oxygenated  $\text{H}_2\text{SO}_4$  solutions,  $\phi(U^{IV})$  was almost one-half of that in the deaerated solution, indicating the effect

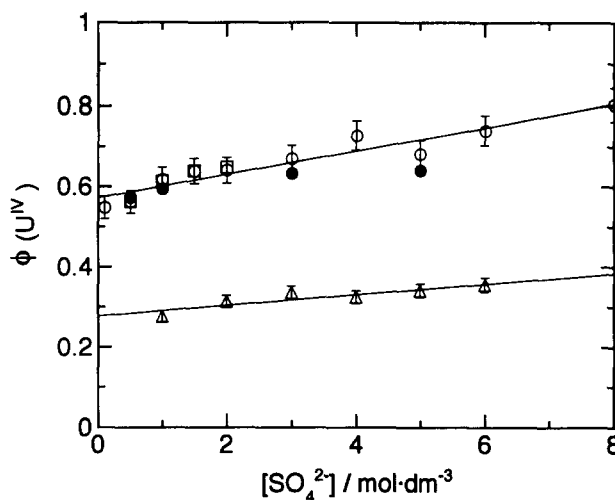
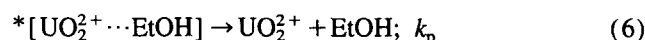
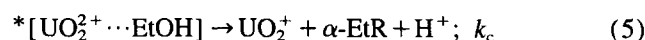
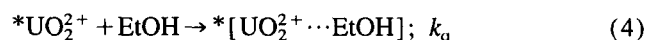


Fig. 2. Dependence of  $\phi(U^{IV})$  on  $[\text{SO}_4^{2-}]$ :  $[\text{H}_2\text{SO}_4]$ , deaerated (○) and oxygenated (△);  $[\text{SO}_4^{2-}]$  ( $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$ , □);  $k_c/(k_c + k_p)$  calculated from Fig. 3 (●). The solution containing  $1.5 \text{ mol EtOH dm}^{-3}$  was irradiated with  $407 \pm 6 \text{ nm}$  exciting light at  $20 \pm 2^\circ \text{C}$ .

of  $\text{O}_2$  on the photoreduction. The effect was also observed in  $\text{UO}_2^{2+}$ –isopropanol system [12].

### 3.2. Photoreduction mechanism of $\text{UO}_2^{2+}$ with EtOH

According to the experimental results of  $\phi(U^{IV})$  at various  $[\text{EtOH}]$  and  $[\text{SO}_4^{2-}]$ , the following deactivation processes of  $^*\text{UO}_2^{2+}$  were proposed on the basis of formation of an encounter complex between  $^*\text{UO}_2^{2+}$  and EtOH [8–11]:

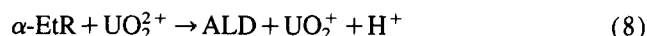
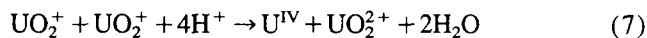


Here  $^*[\text{UO}_2^{2+} \cdots \text{EtOH}]$  indicates an imaginary cage, immediately leading to the alternative quenching routes of  $^*\text{UO}_2^{2+}$ : the chemical quenching which forms  $\text{UO}_2^{2+}$  and  $\alpha\text{-EtR}$ ; the physical quenching where the cage is thermalized collisionally or vibrationally into  $\text{UO}_2^{2+}$  and EtOH. The reverse reaction of reaction (4) was not taken into account as suggested by Butter and Kemp [10], because the intermediate  $^*[\text{UO}_2^{2+} \cdots \text{EtOH}]$  has not been observed yet spectrophotometrically or fluorimetrically.

The resultant  $\alpha\text{-EtR}$  indicates the  $\alpha$ -hydroxyalkyl radical ( $\text{CH}_3\text{CHOH}$ ), which is formed by abstraction of an H atom from the  $\alpha\text{-CH}$  bond of EtOH. On electron spin resonance (ESR) spectra with a  $\text{UO}_2^{2+}$ –EtOH matrix at  $77 \text{ K}$  under photoirradiation [20, 21], only the  $\alpha\text{-EtR}$  has been observed, while 84.3%, 13.2%, and 2.5% of radicals from EtOH are respectively  $\alpha\text{-EtR}$ ,  $\beta\text{-EtR}$  ( $\text{CH}_2\text{CH}_2\text{OH}$ ), and  $\text{CH}_3\text{CH}_2\text{O}$  formed by a radiolytic reaction of EtOH with OH radical

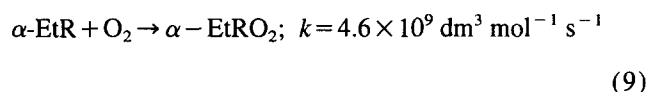
[22]. These facts seem to support that a selective coordination of EtOH to  $^*UO_2^{2+}$  due to the polarity of EtOH [15] is more important in the formation of  $\alpha$ -EtR than H abstraction from EtOH by OH radical derived from  $H_2O$  around  $^*UO_2^{2+}$ , which is highly reactive and not directional.

The resultant  $UO_2^+$  disproportionates quantitatively in the present acid range [23,24].  $\alpha$ -EtR is well known to be a reducing agent in the radiation chemistry and ready to reduce  $UO_2^{2+}$  into  $UO_2^+$  in the  $UO_2^{2+}$ -EtOH system [25,26]:



where ALD indicates acetaldehyde ( $CH_3CHO$ ). Concerning the formal potentials of  $\alpha$ -EtR and uranium ions,  $E^0[(\text{ALD}, H^+)/\alpha\text{-EtR}] = -1.25$  V (vs. normal hydrogen electrode (NHE), pH 0) [27] and  $E^0(UO_2^{2+}/UO_2^+) = +0.16$  V [28] allow the reaction (8). Reactions of  $\alpha$ -EtR with  $UO_2^+$  and  $U^{IV}$  would be also expected from  $E^0(UO_2^+/U^{IV}) = +0.39$  V and  $E^0(U^{IV}/U^{III}) = -0.577$  V [28] and, in fact,  $U^{III}$  is formed at high dose in radiolytic experiments [25,26]. However, in the present experiments those reactions did not take place because the steady state concentration of  $UO_2^+$  is very low in the present  $[H^+]$  range and  $[U^{IV}]$  formed in the photoreduction is less than 10% of the initial  $[UO_2^{2+}]$  as mentioned above. Also, because of the low steady state concentration of  $\alpha$ -EtR in the  $H_2SO_4$  solutions containing  $UO_2^{2+}$  both the disproportionation and dimerization of a pair of  $\alpha$ -EtR [30] should be negligible.

In the oxygenated solutions,  $\alpha$ -EtR prefers a reaction with  $O_2$  to that with  $UO_2^{2+}$ , while  $UO_2^+$  is not likely to react with  $O_2$  because of a small difference between  $E^0(UO_2^{2+}/UO_2^+)$  [28] and  $E^0(H^+, O_2/HO_2) = +0.12$  V [29]:



Hydrogen peroxide results from a successive reaction between a pair of peroxy radicals  $\alpha$ -EtRO<sub>2</sub> after reaction (9) [30] but can hardly oxidize  $U^{IV}$  in the present pH range [31].

### 3.3. Expression of $\phi(U^{IV})$ based on the photoreduction mechanism

On the basis of the above photoreduction mechanism, the yield  $\phi_d(U^{IV})$  of  $U^{IV}$  under deaerated conditions could be expressed in terms of the above rate constants of the deactivation of  $^*UO_2^{2+}$ :

$$\phi(U^{IV}) = \frac{k_q[\text{EtOH}]}{k_0 + k_F + k_q[\text{EtOH}]} \frac{k_c}{k_c + k_p} \quad (10)$$

$$= \frac{K_{SV}[\text{EtOH}]}{1 + K_{SV}[\text{EtOH}]} \frac{k_c}{k_c + k_p} \quad (11)$$

$$K_{SV} = k_q\tau_0 \quad (11)$$

where  $K_{SV}$  and  $\tau_0$  are the Stern–Volmer constant for the quenching of  $^*UO_2^{2+}$  by EtOH and the lifetime of  $^*UO_2^{2+}$  in the absence of EtOH respectively.

When  $[\text{EtOH}]$  in the solutions is so high that the quenching of  $^*UO_2^{2+}$  by EtOH would become predominant among the deactivations as mentioned above, the first term of Eq. (10) should be almost unity because the rate  $k_q[\text{EtOH}]$  is higher than the other rates. The maximum value of  $\phi(U^{IV})$  at higher  $[\text{EtOH}]$  in Fig. 1(b) is found to indicate the second term of Eq. (10),  $k_c/(k_c + k_p)$ , i.e. the ratio of the chemical quenching to the total (chemical and physical) quenching by EtOH. Furthermore,  $\phi_d(U^{IV})$  in Fig. 2 shows that  $k_c/(k_c + k_p)$  depends on  $[SO_4^{2-}]$  potentially.

The yield  $\phi_o(U^{IV})$  of  $U^{IV}$  under oxygenated conditions could be expressed by  $\phi_d(U^{IV})$  multiplied by a factor of 1/2, which agreed well with the results in Fig. 2. This indicates that  $\alpha$ -EtR selectively reacts with  $O_2$  in the oxygenated solutions.

The double-reciprocal plot of  $[\phi_d(U^{IV})]^{-1}$  vs.  $[\text{EtOH}]^{-1}$  has been commonly used to understand the correlation between  $\phi(U^{IV})$  and the quenching of  $^*UO_2^{2+}$ . Eq. (10) can be transformed into the following equation:

$$[\phi_d(U^{IV})]^{-1} = (1 + k_p/k_c) \cdot (1 + K_{SV}^{-1}[\text{EtOH}]^{-1}) \quad (12)$$

where the intercept and slope of the plot could give the kinetic parameters  $k_c/(k_c + k_p)$  and  $K_{SV}$  for the quenching of  $^*UO_2^{2+}$  by EtOH explicitly. Fig. 3 shows the plot in the deaerated  $H_2SO_4$  solutions. The  $k_c/(k_c + k_p)$  and  $K_{SV}$  ( $k_q$ ) values were calculated from the plots at  $[H_2SO_4] = 0.5, 1.0, 3.0,$  and  $5.0 \text{ mol dm}^{-3}$  as shown in Table 1. The  $k_c/(k_c + k_p)$  values were included in Fig. 2 and are found to correspond to the experimentally obtained  $\phi(U^{IV})$  as mentioned above. The correspondence in the photoreduction experiments would assure us of the validity of Eq. (10) in the expression of  $\phi(U^{IV})$ .

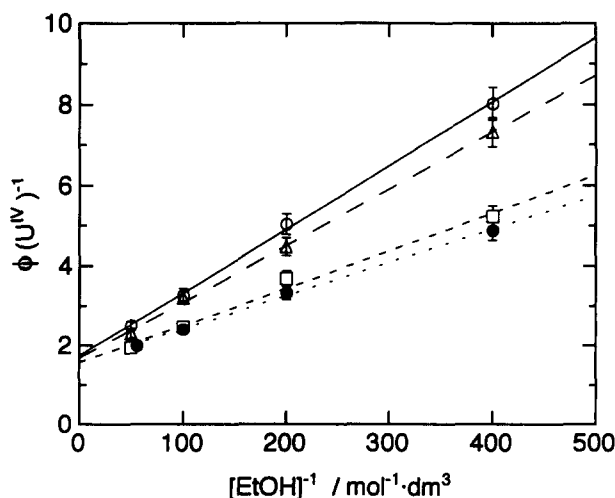


Fig. 3. Double-reciprocal plots of  $[\phi(U^{IV})]^{-1}$  vs.  $[\text{EtOH}]^{-1}$ :  $[H_2SO_4] = 0.5 \text{ mol dm}^{-3}$  ( $\circ$ ),  $1.0 \text{ mol dm}^{-3}$  ( $\Delta$ ),  $3.0 \text{ mol dm}^{-3}$  ( $\square$ ), and  $5.0 \text{ mol dm}^{-3}$  ( $\bullet$ ). The solution was irradiated with  $407 \pm 6 \text{ nm}$  exciting light at  $20 \pm 2^\circ \text{C}$  under deaerated conditions.

Table 1  
The quenching parameters in H<sub>2</sub>SO<sub>4</sub>–EtOH systems <sup>a</sup>

[H <sub>2</sub> SO <sub>4</sub> ] (mol dm <sup>-3</sup> )	Intercept	Slope (mol dm <sup>-3</sup> )	$\frac{k_c}{k_c + k_p}$	$K_{SV}$ (dm <sup>3</sup> mol <sup>-1</sup> )	$\phi(U^{IV})$ <sup>b</sup>	$K_{SV}$ <sup>c</sup> (dm <sup>3</sup> mol <sup>-1</sup> )	$K_{SV}$ <sup>d</sup> (dm <sup>3</sup> mol <sup>-1</sup> )
0.5	1.75	1.58	0.57	110	0.56	119	121
1.0	1.69	1.41	0.59	119	0.61	143	166
3.0	1.59	0.94	0.63	169	0.67	180	235
5.0	1.56	0.83	0.64	191	0.68	215	329

<sup>a</sup> Errors for numerical results shown in this table are within 5%, i.e. three or fewer significant figures.

<sup>b</sup> The experimental quantum yields were obtained in H<sub>2</sub>SO<sub>4</sub> solutions containing 1.5 mol EtOH dm<sup>-3</sup> as shown in Fig. 2.

<sup>c</sup>  $K_{SV}$  values were calculated from the Stern–Volmer plots of photoemission of \*UO<sub>2</sub><sup>2+</sup> at [UO<sub>2</sub><sup>2+</sup>] = 50 mmol dm<sup>-3</sup> as shown in Fig. 4.

<sup>d</sup>  $K_{SV}$  values were calculated from the Stern–Volmer plots at [UO<sub>2</sub><sup>2+</sup>] = 10 mmol dm<sup>-3</sup>.

#### 3.4. Analysis of the photoemission from \*UO<sub>2</sub><sup>2+</sup>

In order to understand the photoreduction mechanism in detail and to check the kinetic parameters for the quenching of \*UO<sub>2</sub><sup>2+</sup> by EtOH derived from  $\phi(U^{IV})$ , additional experiments on the photoemission from \*UO<sub>2</sub><sup>2+</sup> were made by use of a steady state or time-resolved exciting light.

The Stern–Volmer constant  $K_{SV}$  [32] for the quenching of \*UO<sub>2</sub><sup>2+</sup> has been obtained on the basis of the Stern–Volmer equation:

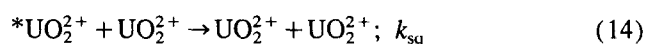
$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[\text{EtOH}] \quad (13)$$

where  $I$  and  $\tau$  are the intensity and lifetime of the emission. The subscript 0 denotes the emission in the absence of EtOH.

Fig. 4 shows the Stern–Volmer plots in H<sub>2</sub>SO<sub>4</sub> solutions, where the emission intensity of \*UO<sub>2</sub><sup>2+</sup> was integrated over the wavenumber range of the emission spectrum of \*UO<sub>2</sub><sup>2+</sup> and measured at the same [UO<sub>2</sub><sup>2+</sup>] = 50 mmol dm<sup>-3</sup> as for the photoreduction. From the slopes of the plots, we obtained the  $K_{SV}$  values shown in Table 1, which agreed well with those obtained from Fig. 3. Thus, the validity of Eq. (10) for  $\phi(U^{IV})$  was confirmed from both the photoreduction and the photoemission experiments. Also,  $K_{SV}$  at [UO<sub>2</sub><sup>2+</sup>] = 10 mmol dm<sup>-3</sup> and the same [H<sub>2</sub>SO<sub>4</sub>] were obtained as shown in Table 1; these were larger than those at [UO<sub>2</sub><sup>2+</sup>] = 50 mmol dm<sup>-3</sup>. This suggests that the self-quenching of \*UO<sub>2</sub><sup>2+</sup> by UO<sub>2</sub><sup>2+</sup> in the excited and/or ground state occurs [1,33].

In order to evaluate the rate constant  $k_q$  for the quenching of \*UO<sub>2</sub><sup>2+</sup> by EtOH from  $K_{SV}$ ,  $\tau_0$  is necessary as shown in Eq. (11).  $\tau_0$  was obtained by a single exponential fitting of the emission decay at the peak wavelengths ( $\lambda_{em}$  = 493, 515, and 538 nm) by use of the pulsed laser. Fig. 5 shows  $\tau_0$  at various [UO<sub>2</sub><sup>2+</sup>] in H<sub>2</sub>SO<sub>4</sub> solutions.

$\tau_0$  at the same [UO<sub>2</sub><sup>2+</sup>] increased linearly with [H<sub>2</sub>SO<sub>4</sub>] as well as perchloric acid concentration [19,34,35], while UO<sub>2</sub><sup>2+</sup> has  $\tau_0$  corresponding to the chemical forms of its hydrates or complexes which mainly exist at specified salt and proton concentrations in carbonate [19] and phosphate [34] solutions. Such an [H<sub>2</sub>SO<sub>4</sub>] dependence of  $\tau_0$  seems to reflect that of  $\phi(U^{IV})$ . On the contrary,  $\tau_0$  decreased with increase in [UO<sub>2</sub><sup>2+</sup>] at the same [H<sub>2</sub>SO<sub>4</sub>], obviously revealing the self-quenching of \*UO<sub>2</sub><sup>2+</sup> as mentioned above:



$$\tau_0^{-1} = k_0 + k_F + k_{sq}[UO_2^{2+}] \quad (15)$$

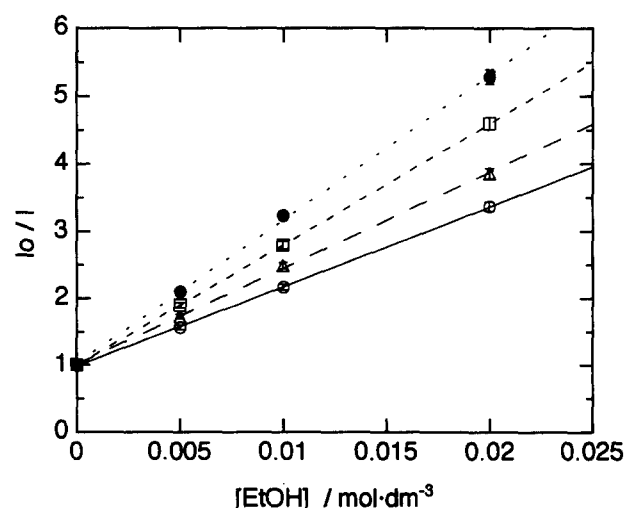


Fig. 4. Stern–Volmer plots of the quenching of \*UO<sub>2</sub><sup>2+</sup> by EtOH: [H<sub>2</sub>SO<sub>4</sub>] = 0.5 mol dm<sup>-3</sup> (○), 1.0 mol dm<sup>-3</sup> (△), 3.0 mol dm<sup>-3</sup> (□), and 5.0 mol dm<sup>-3</sup> (●). The solution was irradiated with 365 nm exciting light at 20 °C under aerated conditions.

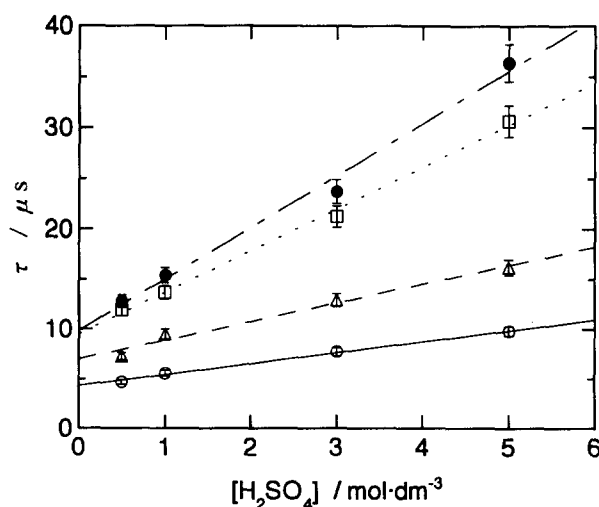


Fig. 5. Lifetimes of \*UO<sub>2</sub><sup>2+</sup> in H<sub>2</sub>SO<sub>4</sub>: [UO<sub>2</sub><sup>2+</sup>] = 0.1 mmol dm<sup>-3</sup> (●), 1.0 mmol dm<sup>-3</sup> (□), 10 mmol dm<sup>-3</sup> (△), and 50 mmol dm<sup>-3</sup> (○). The solution was irradiated with a 266 nm laser pulse at 20 °C under aerated conditions.

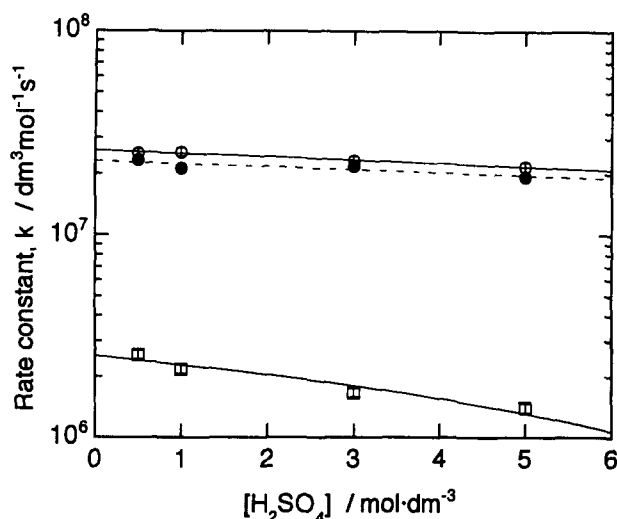


Fig. 6. Rate constants  $k_q$  and  $k_{sq}$  for respectively the quenching of  ${}^*UO_2^{2+}$  by EtOH and the self-quenching by  $UO_2^{2+}$  in  $H_2SO_4$ ;  $k_q$  obtained from the photon emission experiments (O) and the photoreduction experiments (●);  $k_{sq}$  from the photon emission experiments (□).

where  ${}^*UO_2^{2+}$  was assumed to be quenched by  $UO_2^{2+}$  in the ground state.

From the experimentally obtained  $K_{SV}$  and  $\tau_0$ , the rate constants  $k_q$  and  $k_{sq}$  for the quenching of  ${}^*UO_2^{2+}$  by EtOH and  $UO_2^{2+}$  in  $H_2SO_4$  solutions were evaluated as shown in Fig. 6.

$k_q$  was almost constant in the present  $[H_2SO_4]$  range. This shows that the complex  ${}^*[UO_2^{2+} \cdots EtOH]$  could be formed through one selective encounter for EtOH to coordinate to  ${}^*UO_2^{2+}$  after hundreds to thousands of diffusive collisions between  ${}^*UO_2^{2+}$  and EtOH as mentioned above and that changes in hydration and complexation around  ${}^*UO_2^{2+}$  had no influence on the encounter. On the contrary,  $k_{sq}$  decreased slightly from  $(2.6 \pm 0.2) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  ( $0.5 \text{ mol dm}^{-3}$ ) to  $(1.4 \pm 0.1) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  ( $5.0 \text{ mol dm}^{-3}$ ), possibly as a result of effects of viscosity on the diffusive collision, while  $k_{sq} = (4.0 \pm 0.3) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in  $0.233 \text{ mol perchloric acid dm}^{-3}$  solution [33].

The photoreduction derived from the above results can be summarized as follows.  $k_q$ , which indicates the formation rate of the encounter complex, is not influenced by the change around  ${}^*UO_2^{2+}$  such as hydration or complexation, i.e. kinds of solutions. On the contrary,  $k_c/(k_c + k_p)$ , which indicates the ratio of the chemical quenching to the total quenching of  ${}^*UO_2^{2+}$  by EtOH after the encounter complex formed, is influenced mainly by the change in but possibly not by kinds of quenchers for  ${}^*UO_2^{2+}$ .

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