## Reduction of the photoexcited uranyl ion by water 1. $U^{IV}$ and $H_2O_2$ formation

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Photooxidation of water by the uranyl ion was studied. Solutions of uranyl in 0.01-4.0 M H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, or 0.1-1.0 M Na<sub>2</sub>SO<sub>4</sub> and NaClO<sub>4</sub> containing "lacunary" heteropolytungstate (HPT) K<sub>10</sub>P<sub>2</sub>W<sub>17</sub>O<sub>61</sub> or K<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub> were irradiated with a nitrogen laser, a mercury or xenon lamp, or visible light. Spectrophotometric analysis showed that the irradiation results in the accumulation of U<sup>IV</sup>. Simultaneously the formation of H<sub>2</sub>O<sub>2</sub> proceeds. The quantum yield  $\Phi$  of the reaction increases as the concentration of the acid or salt increases. For aerated solutions of 1 M H<sub>2</sub>SO<sub>4</sub> or 1 M HClO<sub>4</sub>, irradiation by light with  $\lambda = 337.1 \Phi$  is close to (1.5-2)  $\cdot 10^{-3}$ . The irradiation of UO<sub>2</sub><sup>2+</sup> into U<sup>IV</sup>. When the irradiation was carried out in the absence of HPA, U<sup>IV</sup> was not detected, although hydrogen peroxide was observed in the solution.

**Key words:** uranyl, photochemistry, photochemical reaction, redox reaction, heteropolytungstate anions, tungstophosphate, tungstosilicate.

Photoexcited uranyl ion  ${}^{*}\text{UO}_{2}{}^{2^{+}}$  is a strong oxidant (the redox potential of the  ${}^{*}\text{UO}_{2}{}^{2^{+}}/\text{UO}_{2}{}^{+}$  pair is estimated to be 2.7 V<sup>1,2</sup>). The potential of the OH  ${}^{*}$ , H<sup>+</sup>/ H<sub>2</sub>O system in a solution with pH 0 is equal to 2.7 V.<sup>3,4</sup> The agreement between these values indicates that water can be oxidized by the excited UO<sub>2</sub><sup>2+</sup> ion to form the OH  ${}^{*}$  radical. An increase in the luminescence lifetime of uranyl on going from aqueous to heavy-aqueous solutions (isotope effect) could be due<sup>1</sup> to the quenching of the excited state by the hydrogen transfer reaction.

$$UO_2^{2+} + h_V \rightarrow UO_2^{2+} \tag{1}$$

$$UO_2^{2+} + H_2O \rightarrow UO_2H^{2+} + OH^{-}$$
 (2)

In Ref. 5, quenching of the excited state of uranyl was explained by electron transfer from a water molecule to uranyl:

$$^{*}\text{UO}_{2}^{2+} + \text{H}_{2}\text{O} \rightarrow \text{UO}_{2}^{+} + \text{OH}^{+} + \text{H}^{+}.$$
 (3)

It was proposed that an electron undergoes intramolecular transfer-involving ligands coordinated around the uranium atom (the reaction along the "equator" of the uranium ion), and the intermolecular transfer of the H atom to the O atom occurs on "poles."<sup>2</sup> All of the available works indicate that the OH<sup>+</sup> radical is formed in the reaction of  ${}^{*}\text{UO}_{2}{}^{2+}$  with H<sub>2</sub>O irrespective of whether the electron or H transfer mechanisms are operative.

The question of whether the interaction of the uranyl excited with water can result in the quenching of luminescence and also in the formation of chemical products remains unclear. This problem is important because most photoreactions of uranyl are performed in aqueous solutions. It attracts interest also regarding water photodecomposition.<sup>6</sup> However, only the private communication on the formation of  $U^{IV}$  during photolysis of phosphate solutions of uranyl is cited in Ref. 7. Based on the chemiluminescence studies of an UV-photolyzed sulfate solution of uranyl, the authors of Ref. 8 suggested  $U^{IV}$  and  $H_2O_2$  as the photolysis products.

However, since the concentrations of these products are insignificant ( $<10^{-5}$  mol L<sup>-1</sup>), they were identified by the data obtained from the studies of the chemiluminescence kinetics. Nevertheless, the authors of the earlier work<sup>8</sup> believe that the OH<sup>+</sup> radical is formed in the primary reactions (1), (2) or (1), (3) followed by the secondary reactions (4) and (5).

$$OH' + OH' \rightarrow H_2O_2, \tag{4}$$

$$2 UO_2^+ + 4 H^+ \rightarrow UO_2^{2+} + U^{4+} + 2 H_2O.$$
 (5)

In this work, we attempted to elucidate the possibility of accumulation of measurable amounts of  $U^{IV}$ during photolysis of  $UO_2^{2+}$  in aqueous solutions.

## Experimental

A weighed sample of crystalline  $UO_2(NO_3)_2$  (reagent grade) was dissolved in twice distilled water, then  $HCIO_4$  was added, and the solution was concentrated until a white vapor appeared.

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 $\text{HClO}_4$  was added to the residue, and the mixture was concentrated again. The wet salt  $\text{UO}_2(\text{ClO}_4)_2$  that formed was dissolved in twice distilled water. This solution was used as the stock solution. The concentration of uranium was determined gravimetrically by precipitating oxide with ammonia and calcining the residue to  $U_3O_8$ . Reagent grades  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ , and their sodium salts were used. Purity of the acids was evaluated by UV spectra. Both acids were optically transparent at  $\lambda \ge 215$  nm. Salts Na<sub>2</sub>SO<sub>4</sub> and NaClO<sub>4</sub> were additionally purified by recrystallization. Unsaturated heteropolytungstates  $K_{10}P_2W_{17}O_{61}$  and  $K_8\text{SiW}_{11}O_{39}$  were synthesized and recrystallized as previously described.<sup>9</sup>

A VIO-1 illuminator with two SVD-120a mercury lamps (the light intensity *I* in the 250-450 nm spectral region was ~ $(1-2) \cdot 10^{16}$  quantum s<sup>-1</sup> cm<sup>-2</sup>) or a DKsSh-500 xenon lamp (in the 250-450 nm region,  $I \approx 7 \cdot 10^{16}$  quantum s<sup>-1</sup> cm<sup>-2</sup>) were used as sources of the UV and visible light. An LGI-505 pulse nitrogen laser ( $\lambda = 337.1$  nm, frequency 1000 Hz, I = $1.5 \cdot 10^{17}$  quantum s<sup>-1</sup>) was used in experiments on measuring the quantum yield. Absorption spectra were recorded on an UV-3100 PC spectrophotometer (Shimadzu, Japan). The lifetime of luminescence was determined using an S1-70 oscillograph with an LGI-505 laser as a light source.

Actinometry was carried out by the ferrioxalate method.<sup>10</sup> The concentration of U<sup>IV</sup> was determined spectrophotometrically by measuring the light absorption of its complexes with heteropolyanions  $P_2W_{17}O_{61}^{-10-}$  or  $SiW_{11}O_{39}^{S-}$ . These complexes have the characteristic spectra; in the case of  $U(P_2W_{17}O_{61})_2^{16-}$ , the bands lie at 692 and 520 nm (for 2 M  $HNO_3 \varepsilon \sim 400$  and 1000 L mol<sup>-1</sup> cm<sup>-1</sup>, respectively<sup>11</sup>). Hydrogen peroxide was determined directly in irradiated uranyl solutions by the procedure based on the use of solutions of potassium iodide and biphthalate12 and measurement of the absorption of the  $l_3^-$  ion that formed in the solution under examina-tion ( $\lambda_{max} = 350$  nm). Since uranyl absorbs in the same region as  $I_3^{-1}$ , the reactants (solutions of potassium iodide and biphthalate) were simultaneously added to irradiated and nonirradiated uranyl solutions, the mixtures were stored for 3 min in the dark, and absorption spectra were recorded (the uranyl ion oxidizes the iodide ion in the light, interfering with the results of analysis). After subtracting the spectra of non-irradiated samples from the spectra of irradiated solutions, the spectrum of the absorption of the  $I_3^-$  ion was obtained, and then the amount of H<sub>2</sub>O<sub>2</sub> in the irradiated solution was calculated from the intensity of a maximum at 350 nm. In several cases, an accuracy of determination was monitored by adding  $H_2O_2$  to a sample under analysis. The estimation of the effect of interfering factors (the need to subtract the spectra, the presence of  $U^{IV}$  in the sample, etc.) showed that  $H_2O_2$  can be determined by this method with an error below  $\pm 20\%$ . The concentration of H2O2 was determined in perchlorate solutions (pH 2-4), in which only H<sub>2</sub>O<sub>2</sub> was formed as an oxidant during photolysis. It was impossible to analyze strongly acidic solutions by this method. All experiments were carried out at 20±2 °C.

## **Results and Discussion**

In preliminary experiments aimed at determining molar extinction coefficients of the U<sup>IV</sup> complexes with HPT in 0.1 M H<sub>2</sub>SO<sub>4</sub>, we carried out the quantitative photoreduction of the uranyl ion by ethanol. The absorption spectra of the solutions obtained after U<sup>IV</sup> ceased to accumulate are presented in Fig. 1. In the

Fig. 1. Absorption spectra of  $U(SiW_{11}O_{30})_2^{12-}$  (1) and  $U(P_2W_{17}O_{51})_2^{16-}$  (2) complexes in 0.1 M H<sub>2</sub>SO<sub>4</sub>. [U<sup>IV</sup>] =  $2 \cdot 10^{-4}$  mol L<sup>-1</sup>, [HPT] =  $10^{-3}$  mol L<sup>-1</sup>.

case of the  $U(P_2W_{17}O_{61})_2^{16-}$  complexes, the bands at 694 and 520 nm ( $\epsilon = 380\pm20$  and 950 $\pm70$  L mol<sup>-1</sup> cm<sup>-1</sup>) can be used for analytical purposes; the spectrum obtained virtually coincides with that presented previously.<sup>11</sup> The spectrum of  $U(SiW_{11}O_{39})_2^{12-}$  contains a band with a maximum at 692 nm ( $\epsilon = 200\pm15$  L mol<sup>-1</sup> cm<sup>-1</sup>) and a shoulder near 512 nm ( $\epsilon = 700\pm50$  L mol<sup>-1</sup> cm<sup>-1</sup>). These complexes have similar spectra in other media.

On examining the photochemical reactions of the uranyl with water, a solution with a  $UO_2^{2+}$  concentration of 1-20 mmol  $L^{-1}$  in a glass cell (l = 2 cm,volume 10 mL) was irradiated with UV light from a DKsSh-500 lamp. A 0.01-1.0 M solution of HClO<sub>4</sub>.  $0.005 - 3.8 M H_2SO_4$ , or sodium salts of these acids with concentrations to 1 mol  $L^{-1}$  were used as supporting electrolytes. After irradiation for  $\leq 2$  h,  $7 \cdot 10^{-4}$  M  $K_{10}P_2W_{17}O_{61}$  was added to the solution. After 10-15 min, the absorption spectrum was recorded in a 5-cm quartz cell. Counting UIV formed in reaction (5) in experiments performed under these conditions, the total concentration of  $U^V$  and  $U^{IV}$  in the solution did not exceed  $(1-2) \cdot 10^{-6}$  mol L<sup>-1</sup>. When HPT  $(K_{10}P_2W_{17}O_{61})$ or  $K_8SiW_{11}O_{39}$ ) was introduced into the solution before photolysis, a 30-min irradiation yielded an accumulation of  $U^{IV}$  in concentrations of as much as  $(6-8) \cdot 10^{-5}$ mol  $L^{-1}$  U<sup>IV</sup>; when the concentration of the acid or salt decreased, the amount of U<sup>IV</sup> decreased. Accumulation of U<sup>IV</sup> also occurred during photolysis of uranyl solutions effected by the light of a mercury lamp or a nitrogen laser.

These experiments were carried out in the absence of a reducing agent. The results obtained in perchlorate solutions can be explained by the reduction of the photoexcited uranyl ion with water. In sulfate solutions, the photoreduction of  ${}^{1}\text{UO}_{2}^{2+}$  by the HSO<sub>4</sub><sup>-</sup> ions also cannot be ruled out.



HPT that form reduced forms, "blues," also can participate in photoreactions. To reveal the role of HPT, we studied the influence of  $K_8SiW_{11}O_{39}$  on the luminescence lifetime  $\tau$  of uranyl (0.02 *M*) in a 0.1 *M* solution of  $H_3SO_4$ .

{K <sub>8</sub> SiW <sub>11</sub> O	391 0	0.32	0.64	1.0	4.3	10.9
/mmol L <sup>=1</sup> τ/μs	8.6±0.1	8.4±0.1	8.2±0.2	8.0±0.3	6.4-7.26	2-9.0

As can be seen, HPT slightly affects the luminescence of acidic solutions.

The quenching is not described by the Stern-Volmer law; the decay curve does not follow the exponential plot at high  $[K_8SiW_{11}O_{39}]$ . These effects are more pronounced in perchloric acid and especially, at a lower concentration of H<sup>+</sup>. The influence of HPT on luminescence of uranyl is mainly related to complex formation. Similar results were obtained for  $K_{10}P_2W_{17}O_{61}$ . The estimation of the quenching rate constant for the initial region of the decay curve gives  $k \le 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ . This indicates that the intermolecular energy transfer from the uranyl to HPT is not efficient. The presence or absence of the direct photoexcitation of HPT does not play an important role. For example, the photoreduction of uranyl in the presence of  $K_8SiW_{11}O_{39}$  occurred under visible light (irradiation through a ZhS-11 light filter, the onset of transmission at  $\lambda > 400$  nm. 50% transmission at  $\lambda = 420$ nm), which is not absorbed by the heteropolyanion. Complex formation of HPT with uranyl and a change in the oxidation potential of the  $UO_2^{2+}/UO_2^{+}$  pair have no effect on the photoreduction of the  $UO_2^{2+}$  ion. Taking into account the known data for the AmO<sub>2</sub><sup>2+</sup>/AmO<sub>2</sub><sup>+</sup> pair,<sup>13</sup> we can assume that when HPT is added to acidic solutions, the potential of the  $UO_2^{2+}/UO_2^{+}$  pair also should not noticeably change. In acidic solutions containing  $\geq 1 M H^+$ , at HPT concentrations  $\leq 10^{-3} mol L^{-1}$ . the complex formation of uranyl with HPT can be neglected<sup>14</sup>; however, in neutral solutions these complexes are rather stable. At the same time, in solutions with the same ionic strength, but different pH, the photoreduction of uranyl occurs with similar rates. We cannot completely exclude the participation of HPT in the photochemical stages, but it is most probable that their role is the fast stabilization of the reduced uranium in the tetravalent state.

The quantum yield was measured in aerated solutions containing 0.02 mol L<sup>-1</sup> uranyl. To decrease the effect of the internal filter, we used the tungstosilicate anion SiW<sub>11</sub>O<sub>39</sub><sup>S-</sup>, which possesses a lower light absorption at 337 nm than that of  $P_2W_{17}O_{61}^{10-}$ . The concentration of K<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub> was  $5 \cdot 10^{-4}$  mol L<sup>-1</sup>, which is sufficient for the stabilization of U<sup>1V</sup> at early stages of the reaction. Figure 2 shows the spectra of light absorption of uranyl in a 1 *M* solution of HClO<sub>4</sub> before and after 30-min irradiation, the difference between these spectra, and the curves of U<sup>IV</sup> accumulation. Similar



Fig. 2. *a*, Absorption spectra of uranyl in 1 *M* HClO<sub>4</sub> in the presence of  $5 \cdot 10^{-4}$  *M* K<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub> before (1) and after (2) 30-min irradiation by a nitrogen laser ( $\lambda = 337.1$  nm). [UO<sub>2</sub><sup>2+</sup>] = 0.02 mol L<sup>-1</sup>. The inset shows the kinetic curves of accumulation of uranium(iv) in 1 *M* H<sub>2</sub>SO<sub>4</sub> (1) and HClO<sub>4</sub> (2). The amount of light (in mEinstein) incident on the cell with the solution during the irradiation time is indicated on the upper scale; *b*, difference in the spectra before and after irradiation related to the accumulation of U<sup>1V</sup>.

**Table 1.** Average quantum yields ( $\Phi$ ) of photoreduction of uranyl by water in the presence of  $5 \cdot 10^{-4} M K_8 SiW_{11}O_{39}$ 

Medium	$\Phi \cdot 10^3$ within <i>t</i> /min				
	i	õ	30		
1.0 M H <sub>2</sub> SO <sub>4</sub>	1.88	1.01	0.32		
0.5 M H <sub>2</sub> SO <sub>4</sub>	1.40	0.82			
0.125 MH-SO4	0.67	0.40			
0.01 <i>M</i> H <sub>2</sub> SO <sub>4</sub>	~0.5	0.29	-		
0.005 M H <sub>2</sub> SO <sub>3</sub> +					
$+ 0.5 M Na_2 SO_1$	1.83	1.03			
1.0 M HClO4	1.74	1.18	0.62		
0.01 M HCIO <sub>4</sub> +					
+ 1 $M$ NaClO <sub>4</sub>	1.70	1.13			

Note.  $[UO_2^{2+}] = 0.02 \text{ mol } L^{-1}$ , pulse of nitrogen laser,  $\lambda = 337.1 \text{ nm.}$ 

UIV · 105/mmol

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Fig. 3. Kinetics of reduction of uranyl by water in solutions with different concentrations of  $H_2SO_4$  (*I*-5) and in 0.5 *M* Na<sub>2</sub>SO<sub>4</sub> (6, 7). Irradiation by light with  $\lambda \ge 360$  nm, intensity (region of 370–450 nm) ~2.5 \cdot 10^{16} quantum s<sup>-1</sup> cm<sup>-2</sup>. [UO<sub>2</sub><sup>2+</sup>] = 0.02 mol L<sup>-1</sup>, [SiW<sub>11</sub>O<sub>39</sub><sup>8-</sup>] = 5 \cdot 10<sup>-4</sup> mol L<sup>-1</sup>. [H<sub>2</sub>SO<sub>4</sub>]/mol L<sup>-1</sup>: 0.01 (*I*), 0.1 (*2*), 0.5 (*J*), 1.0 (4), and 4.0 (5); [Na<sub>2</sub>SO<sub>4</sub>] at pH 2 (6) and 4 (7).

results were obtained for other solutions. Based on the above presented data and taking into account the fraction of the light absorbed by the uranyl ion, we calculated the quantum yield ( $\Phi$ ) of the reaction ( $\lambda = 337.1$  nm). The error of determination was  $\pm 15\%$ . The results are presented in Table 1.

The reaction rate rapidly decreases in the course of photolysis. This is related in part to an increase in the effect of an internal filter due to the absorption of the uranium(iv) complexes. However, the quantum yield decreases simultaneously and rapidly. This is due to the inverse reactions. At the same concentration of the H<sup>+</sup> ions, the quantum yields in perchloric and sulfuric acids differ insignificantly, despite the fact that in sulfuric acid uranyl forms complexes with sulfate ions. A decrease in the acid concentration results in a decrease in

the quantum yield. It is of interest that the quantum yield is affected by the ionic strength rather than by the concentration of hydrogen ions. In  $0.5-1.0 \ M$  solutions of salts with pH ~ 2 or pH ~ 4-5, the reaction proceeds almost in the same way as in  $0.5-1.0 \ M$  acids.

Similar values of the quantum yields in  $HClO_4$  and  $H_2SO_4$  apparently indicate that mechanisms of these reactions are independent of the nature of the anion in the solution. However, the light absorption of the uranyl sulfate complexes is much higher, and the rate of  $U^{IV}$  accumulation is higher. This prompted us to perform some experiments in a sulfate medium.

A decrease in the reaction rate during photolysis is also observed when uranyl solutions are photoirradiated by a DKsSh-500 lamp with a BS-7 filter (transmission at  $\lambda \ge 360$  nm, *i.e.*, in the region with the absorbance solely due to the uranyl ion and accumulating  $U^{(V)}$  (Fig. 3). Curves similar to those shown in Fig. 3 were also observed for perchloric solutions. In acidic solutions, the reaction rate is reduced more strongly than in neutral solutions. Perhaps, this is related to a lower stablity of the  $U^{IV}$  complexes in the acidic medium and a more efficient contribution from reverse reactions of uranium(iv). The accumulation of U<sup>IV</sup> continues until HPT is present in the solution. We performed an extended irradiation of 0.001 M solutions of uranyl in the presence of  $K_8 SiW_{11}O_{39}$ in a 0.5 M solution of Na<sub>2</sub>SO<sub>4</sub> (pH  $\sim$  4). Under these conditions, the  $SiW_{11}O_{39}^{3-}$  anion is thermodynamically stable, whereas in the highly acidic medium,  $SiW_{11}O_{39}^{8-}$ and  $P_2 W_{17} O_{61}^{10-}$  are slowly transformed into the corresponding saturated heteropolyanions of the 12 and 18 series.<sup>9</sup> As can be seen from the data presented below, after tens of hours of irradiation with the light from a VIO-1 source. >80% of the uranyl ions are reduced.

₹/h	U <sup>IV</sup> (%)	τ/h	U <sup>IV</sup> (%)
1.5	4.0	63	46.3
4.5	9.0	81	56.5
9	14.5	119	68.0
20	23.4	140	75.0
33	30.8	179	80.4
49	39.5	240	83.0

**Table 2.** Accumulation of  $U^{1V}$  and  $H_2O_2$  during photolysis of uranyl in a solution containing 0.5 M NaClO<sub>4</sub> and 0.01 M HClO<sub>4</sub> in the presence and absence of K<sub>8</sub>SiW<sub>+1</sub>O<sub>39</sub>

Irradia-	····	· · · · · ·	$[K_8 SiW_{11}O_{39}]/mol L^{-1}$		· · · ·			
tion	5.10-4		2.10-4			0		
time	$[U^{IV}] \cdot 10^5$	$[H_2O_2] \cdot 10^5$	$[U^{VV}] \cdot 10^5$	$[H_2O_2] \cdot 10^5$		)5		
/min					1*	2*	3*	
4	0.4	1.0			~0.7		~0.6	
15	1.0	1.9	0.7	1.2	1.5	1.5	1.4	
40	1.5	2.6	1.3	1.9	1.5	2.3	1.7 (1.3**)	
75		_		-	3.8	_	1.4 (1.1**)	
90	3.1	3.6	3.0	4.0	_	2.0	1.4 (1.1**)	
120	3.8	4.0	3.2	4.1	-	1.6		

*Note.* Irradiation by the light of a DKsSh-500 lamp without light filters.  $[UO_2^{2+}] = 0.02 \text{ mol } L^{-1}$ . \* Number of experiment. \*\* Estimated from the data on reduction of Np<sup>VI</sup>.



Fig. 4. Absorption spectra of a solution containing 0.02 M uranyl in a mixture of 0.5 M NaClO<sub>4</sub> and 0.01 M HClO<sub>4</sub> after the addition of potassium biphthalate and iodide. *I*, Initial uranyl solution; 2, uranyl solution irradiated within 30 min; 3, difference between spectra 2 and *I*; and 4, standard aqueous solution of  $H_2O_2$ .

Taking into account that dissolved oxygen can participate in some reactions of uranium, we compared the initial rate of accumulation of  $U^{1V}$  in 0.2 *M* Na<sub>2</sub>SO<sub>4</sub>, pH ~ 4, for solutions saturated with argon, air, and oxygen. The ratio of the rates was 1.53 : 1.00 : 0.93. Thus, the removal of O<sub>2</sub> from the solution results in an increase in the yield of uranyl photoreduction, most likely, due to a reduced contribution from the reverse oxidation of uranium(v) by oxygen.

As follows from the published data,<sup>8</sup> hydrogen peroxide is a product of oxidation of water by uranyl. We carried out a series of experiments to determine U<sup>1V</sup> along with  $H_2O_2$  produced by the photoirradiation of uranyl solutions. The experiments were carried out in a solution containing 0.5 *M* NaClO<sub>4</sub> and 0.01 *M* HClO<sub>4</sub>, because in a sulfate solution the formation of  $S_2O_8^{2-1}$ ions cannot be excluded. At pH  $\ge$  5,  $H_2O_2$  can form peroxide complexes with uranyl.<sup>15</sup> Under our experimental conditions, this process can be neglected. For analysis a solution of uranyl (0.2 mL) was sampled, then water (0.3 mL) and a mixed iodide-biphthalate solution (0.5 mL) were added, and absorption spectra were recorded in a 1-cm cell. An example of determination of  $H_2O_2$  is presented in Fig. 4, and the results obtained are collected in Table 2.

In the irradiated sulfate solutions, we also observed products that oxidize  $I^-$  and initiate the formation of  $I_3^-$ ; however, it is probable that this is due in part to the appearance of  $S_2O_8^{2-}$  ions, which enter into the reaction with iodide.

The formation of  $H_2O_2$  was detected in all experiments, including those conducted in the absence of

HPT. In this case, hydrogen peroxide was identified in parallel by the second method: an aliquot of neptunium(vi) was added to irradiated and non-irradiated solutions. In an acidic medium, neptunium(vi) readily reacts with  $H_2O_2$  to form  $Np^V$  (see Ref. 16, p. 490), which has a characteristic maximum at 981 nm ( $\epsilon = 400 \text{ L mol}^{-1} \text{ cm}^{-1}$ , see Ref. 16, p. 484). In all cases, when peroxide was detected by the iodidebiphthalate method, Np<sup>VI</sup> was also reduced in the irradiated solution. The concentration of  $Np^{V}$  was ~2 times higher than that of  $H_2O_2$ , which is explained by the fact that one peroxide molecule reduces two Np<sup>VI</sup> ions. A combination of the oxidative (interaction with iodide) and reductive (formation of  $Np^{V}$ ) properties of the products of photolysis of uranyl indicates that this product is  $H_2O_2$ .

The  $[H_2O_2]$  value in the process apparently achieves a stationary level close to a value of  $n \cdot 10^{-5}$  mol L<sup>-1</sup>. The  $U^{V}$  formed is unstable; it disproportionates and is oxidized by hydrogen peroxide and oxygen. In the absence of HPT, uranium(iv) that is formed during disproportion of uranium(v) is unstable and efficiently oxidized in both dark and photochemical reactions. The presence of absorption bands in both the visible and UV spectral regions provides evidence for a facile oxidation of U<sup>V</sup>. In this case,  $H_2O$  ( $H_2O_2$ ) can serve as a photooxidant of U<sup>IV</sup>, whereas U<sup>VT</sup> and hydrogen (or H<sub>2</sub>O) are most likely reaction products. No noticeable accumulation of  $U^{IV}$  is observed in the solution in the absence of HPT, although the decomposition of water does occur. Along with reactions involving uranium in lower oxidation states, hydrogen peroxide interacts with excited uranyl,<sup>17</sup> and dioxygen is the final product of the reactions (reactions (7), (10)-(12)). In the presence of HPT, U<sup>IV</sup> is bound to form a complex that is more resistant toward the inverse photooxidation.

Thus, in the systems under study, uranyl serves as an oxidant for photochemical oxidation of water. Probably, the accumulation of  $U^{1V}$  in the presence of HPT includes the following main steps.

$$2 UO_2^{2+} + 2 H_3O^+ + hv \rightarrow$$
  
$$\rightarrow UO_2^{2+} + U^{|V|} + H_2O_2 + 2 H_2O$$
(6)

The mechanism of this reaction includes the primary act (it is not considered hereinafter) and the disproportionation of  $U^{V}$ . In the presence of HPT, uranium(IV) forms a complex with it to attain some stabilization. When sufficient amounts of peroxide are accumulated, the latter begins to enter into the photoreaction with uranyl, the dark reaction with  $U^{V}$  (Ref. 17), and, most likely, the reaction with  $U^{IV}$ , even if the latter exists in the solution as a complex with HPT<sup>18</sup>:

$$UO_2^{2+} + H_2O_2 \rightarrow UO_2^{+} + H^+ + HO_2.$$
 (7)

$$UO_2^+ + H_2O_2 + H^+ \rightarrow UO_2^{2+} + OH^- + H_2O,$$
 (8)

$$J^{V} + H_2 O_2 \to U O_2^{2+} + 2 H^+.$$
 (9)

To reveal the role of  $H_2O_2$ , we measured the quantum yield of photoformation of U<sup>IV</sup> in 1 *M* HClO<sub>4</sub> in

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Fig. 5. Kinetics of photoreduction of uranyl in 1 *M* HClO<sub>4</sub> in the presence of  $5 \cdot 10^{-4}$  *M* K<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub>, laser irradiation,  $\lambda = 337.1$  nm. [H<sub>2</sub>O<sub>3</sub>] = 0 (1) and 0.01 (2) mol L<sup>-1</sup>.

the presence of HPT at  $[H_2O_2] = 0.01 \text{ mol} \text{L}^{-1}$  (Fig. 5). The initial stage, at which the reaction proceeds much faster than in the absence of peroxide, is characterized by a quantum yield equal to ~0.03. Then the photoformation of U<sup>IV</sup> is very rapidly retarded to proceed with approximately the same rate as that without additives of hydrogen peroxide. This confirms the role of hydrogen peroxide in the reverse reactions involving  $U^{IV}$  and  $U^{V}$ . However, peroxide reacts very slowly with the  $U^{IV}(HPT)_2$  complexes even under the action of light. The experiments showed that the  $U(SiW_{11}O_{39})_2^{12-1}$ complexes were fairly stable toward the photooxidation by  $10^{-3} - 10^{-4}$  M solutions of peroxide both at pH 2 and in 0.5 M HClO<sub>4</sub>. The quantum yield of this process under light with  $\lambda = 337.1$  nm does not exceed  $10^{-4}$ . Probably, during the photolysis of uranyl, the  $U^{IV}$  ions, still not bound in the U<sup>IV</sup>(HPT)<sub>2</sub> complex, enter into the reaction with hydrogen peroxide. In addition, U<sup>IV</sup> is oxidized by the  $OH^-$  radicals that were formed in reaction (8), whereas  $U^V$  is oxidized by the  $OH^-$  radicals and dissolved dioxygen<sup>19</sup>:

$$UO_2^+ + OH^- \rightarrow UO_2^{2+} + OH^-, \tag{10}$$

$$2 UO_2^+ + O_2^- + 2 H^+ \rightarrow 2 UO_2^{2+} + H_2O_2^-.$$
(11)

The OH  $\cdot$  radicals also can recombine, and the HO<sub>2</sub> radicals enter into the reaction

$$HO_2^{-} + HO_2 \rightarrow H_2O_2 + O_2 \tag{12}$$

or form intermediates with uranyl<sup>17,20</sup>.

$$UO_2^{2+} + HO_2 \leftrightarrow UO_2(HO_2)^{2+}.$$
 (13)

which, interacting with the same intermediates and  $HO_2$ , are also decomposed to evolve  $H_2O_2$  and dioxygen<sup>17</sup>:

$$HO_2, UO_2(HO_2)^{2+} \rightarrow H_2O_2, O_2, UO_2^{2+}.$$
 (14)

Dioxygen is the final product of photooxidation of water by uranyl.

Photolysis of  $H_2O_2$  and ions of the medium ( $SO_4^{2^-}$ ,  $ClO_4^-$ ) can be neglected, because when light with  $\lambda \ge 360$  nm is used the contribution of these reactions is low. Evidently, the retardation of accumulation of  $U^{1V}$  during photolysis is related to the formation of  $H_2O_2$  and occurrence of processes (8)—(10). When the time of photolysis increases,  $U^V$  and  $H_2O_2$  are formed in quasi-stationary concentrations, and the rate of  $U^{1V}$  accumulation is stabilized. Peroxide is consumed not only in the oxidation of  $U^{1V}$  and  $U^V$  but also in the photoreduction of uranyl.

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## References

- t. H. D. Burrows and T. J. Kemp, Chem. Soc. Rev., 1974, 3, 139.
- A. L. Buchachenko and I. V. Khudyakov, Usp. Khim., 1991, 60, 1105 [Russ. Chem. Rev., 1991, 60 (Engl. Transl.)].
- H. A. Schwarz and R. W. Dodson, J. Phys. Chem., 1984, 88, 3643.
- 4. U. K. Klänning, K. Schested, and J. Holeman, J. Phys. Chem., 1985, 89, 760.
- M. Moriyasu, Y. Yokoyama, and S. Ikeda, J. Inorg. Nucl. Chem., 1977, 39, 2211.
- 6. V. N. Parmon, in Fotokataliticheskoe preobrazovanie solnechnoi energii [Photocatalytic Conversion of Solar Energy], Ch. 2, Nauka, Novosibirsk, 1985, 6 (in Russian).
- 7. M. D. Marcantonatos, Inorg. Chim. Acta, 1977, 24, L37
- L. A. Khamidullina, S. V. Lotnik, and V. P. Kazakov, *Izv. Akad. Nauk. Ser. Khim.*, 1994, 751 [*Russ. Chem. Bull.*, 1994, 43, 704 (Engl. Transl.)].
- 9. M. P. Souchay, *Polyanions et Polycations*. Gauthier, Paris, 1963.
- C. A. Parker, *Photoluminescence of Solutions*, Elsevier Publishing Company, Amsterdam, 1968.
- 11. L. Bion, Ph. Moisy, and C. Madie, Radiochimica Acta, 1995, 69, 251.
- 12. J. T. Kiwi and M. Daniels, J. Inorg. Nucl. Chem., 1978, 40, 576.
- E. A. Erin, A. A. Baranov, A. Yu. Volkov, V. M. Chistyakov, and G. A. Timofeev, *Radiokhimiya*, 1995, 37, 115 [*Radiochemistry*, 1995, 37 (Engl. Transl.)].
- 14. J.-M. Adnet, Extraction Selective des Actinides des Effluents de Haute Activite, These, Centre d'Etudes Nucleaire de Fontenay-aux-Roses, 1992.
- 15. J. C. Sullivan, S. Gordon, D. Cohen, W. Mulac, and K. H. Schmidt, J. Phys. Chem., 1976, 80, 1684.
- The Chemistry of the Actinide Elements, Vol. 1, 2nd, Eds. J. J. Katz, G. T. Seabörg, and L. R. Morss, Chapman and Hall, London-New York, 1986.
- 17. Y. Mao and A. Bakac, Inorg. Chem., 1996, 35, 3925.
- L. P. Maslov, L. V. Sirotinkina, and A. G. Rykov, *Radiokhimiya*, 1985, 27, 732 [*Radiochemistry*, 1985, 27 (Engl. Transl.)].
- 19. W.-D. Wang, A. Bakac, and J. H. Espenson, *Inorg. Chem.*, 1995, 34, 6034.
- D. Meisel, Y. A. Ilan, and G. Czapski, J. Phys. Chem., 1974, 78, 2330.

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