

Photostimulated Oxygen Exchange and Photochemical Properties of Uranyl Ions*

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Oxygen uranyl exchange has been studied in connection with problems of the uranyl bond nature [1–3], the nature of the uranyl photoexcited state [4, 5] and isotope enrichment [6]. Crandall [1] found that uranyl oxygen atoms practically do not participate in oxygen exchange with water molecules. This circumstance played a considerable role in the presentation of uranyl as a monolithic particle. Gordon and Taube [4, 7] carried out the first quantitative measurements of uranyl oxygen exchange rate in aqueous solutions. They showed that the exchange proceeded very slowly in acid solutions ($t_{1/2} \sim 10^4$ h) but was strongly accelerated in the presence of reductors (Eu^{2+} , Cr^{2+}), which were capable of transforming uranyl ions into uranoyl (UO_2^+). In accordance with refs. 4 and 7, the latter catalyzes the exchange of uranyl. These authors [4] also found the exchange acceleration on irradiation of uranyl perchlorate solution by ultraviolet light ($\lambda = 254$ nm). They supposed that irradiation led to uranoyl formation also. Later, Fukutomi *et al.* [5] found that visible light ($\lambda = 436$ nm) could also accelerate exchange and measured exchange quantum yield, Φ . These Φ values essentially exceed the unit and do not depend on the light intensity. On the basis of these data [5], the following exchange mechanism was proposed. Oxygen exchange is catalyzed directly by the uranyl in the lowest electronic excited state, not excluding the possibly different nature of the effect of ultraviolet and visible light.

These contradictory presentations about photostimulated oxygen exchange are based on very limited experimental material.

The object of the present work is the investigation of the nature of the exchange centre arising at irradiation and the influence of the different physical and chemical factors on the exchange photostimulation.

Experimental

The new IR spectrophotometrical method of isotope analysis was developed for the oxygen exchange investigation. This method allows determination of both the total ^{16}O and ^{18}O content in uranyl and the content of isotopic forms: $[\text{}^{16}\text{OU}^{16}\text{O}]^{2+}$, $[\text{}^{16}\text{OU}^{18}\text{O}]^{2+}$ and $[\text{}^{18}\text{OU}^{18}\text{O}]^{2+}$ [8]. With this method the intensities of the $\nu_{\text{as}} \text{UO}_2^{2+}$ bands of the different isotopic forms were determined in the spectrum of $\text{NaUO}_2(\text{CH}_3\text{COO})_3$, the latter being deposited from the investigated solutions. The determination error is estimated as 5% in the optimal region of 30–80% ^{18}O content.

$\text{UO}_2(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ was used for the preparation of solutions. Isotope ^{18}O was introduced into the uranyl by prolonged (~ 2 days) storage of the salt solution in the heavy oxygen water at $\text{pH} = 3$ and consequent removal of water under vacuum. The labelled salt was dissolved in aqueous solutions of HClO_4 with the natural oxygen isotope content. The ^{18}O loss in the UO_2^{2+} group describes the exchange process.

The solutions were placed into the cylindrical glass cuvette (10 mm in diameter) with a water jacket. The distilled water passed through the jacket at a constant temperature. The cuvette was placed at the focus of the ellipsoidal mirror and the light source at the other focus. The light source was a high pressure xenon impulse lamp (impulse duration ~ 1 ms, frequency ~ 0.25 Hz and lower) or a mercury lamp of constant action. The glass light filters were placed between the lamp and the cuvette. The light flow was measured by a Parker actinometer filled with potassium ferrioxalate [9]. Dried helium of high purity was bubbled through the solution before and during the irradiation.

The quantum yield of oxygen exchange reaction, Φ , was determined as the ratio of the exchange event number to the number of light quanta absorbed by uranyl ion. Special experiments showed that the ClO_4^- ions do not participate in the oxygen exchange.

The half-exchange time as a function of the solution acidity in the dark is shown in Table I.

Figure 1 shows IR spectra of $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ deposited from a 12 M HClO_4 solution before and after irradiation. Light action diminishes the ^{18}O content in uranyl, the intensities of $\nu_{\text{as}}[\text{}^{16}\text{OU}^{18}\text{O}]^{2+}$ and $\nu_{\text{as}}[\text{}^{18}\text{OU}^{18}\text{O}]^{2+}$ bands being lowered simultaneously.

Figure 2 shows the experimental dependence of the $[\text{}^{16}\text{OU}^{16}\text{O}]^{2+}$, $[\text{}^{16}\text{OU}^{18}\text{O}]^{2+}$ and $[\text{}^{18}\text{OU}^{18}\text{O}]^{2+}$ mole fractions, p_i , on the light impulse number, N (dots), in a 12 M HClO_4 solution, as well as calculated dependences for the case of 'bioxygen' (simultaneous exchange of the two uranyl oxygen

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TABLE I. Kinetics of Uranyl Oxygen Exchange in HClO₄ Solutions in the Dark

C(HClO ₄) (M)	0.01	0.1	1	2	4	6	12
Time (h)	2	505	168	285	208	500	17500
Time of half-exchange (t _{1/2} , h)	4	1 × 10 ³	1.5 × 10 ³	2 × 10 ³	6.6 × 10 ³	exchange is not found	

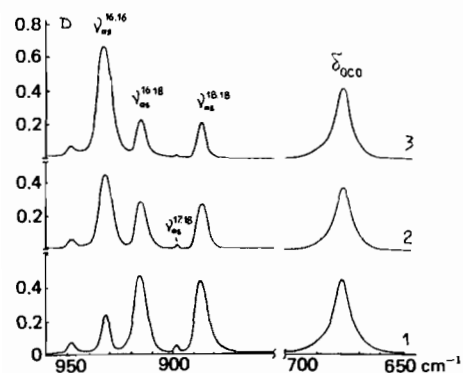


Fig. 1. Fragments of the IR spectrum of NaUO₂(CH₃COO)₃ deposited from solution of UO₂(ClO₄)₂ (C_U = 0.1 M, C(HClO₄) = 12 M, λ_{max} = 400 nm, KBr-matrix, ¹⁸O enrichment in UO₂²⁺ group): (1) up to irradiation; (2) 300 light impulses; (3) 600 light impulses.

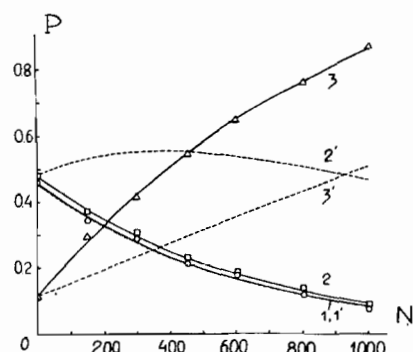


Fig. 2. Ratio of uranyl isotopic forms, p , as a function of light impulse number N (C_U = 0.1 M, C(HClO₄) = 12 M). Calculated p of ¹⁸OU¹⁸O²⁺, ¹⁶OU¹⁸O²⁺ and ¹⁶OU¹⁶O²⁺ forms for bioxygen exchange are lines (1), (2) and (3); for monooxygen exchange, lines (1'), (2') and (3'): ○, □, △ = experimental p values for these forms.

atoms) and 'monooxygen' (independent oxygen atom exchange; it is described by binomial, statistical distribution exchange mechanism). We can see that the practically 'pure' bioxygen exchange mechanism is realised here. Our data show that the bioxygen exchange takes place also in the dark (in acidic solutions).

Figure 3 shows the dependence of Φ on the uranyl concentration at C(HClO₄) = 1 M. Figure 4 shows the dependence of Φ on the solution acidity at C_U =

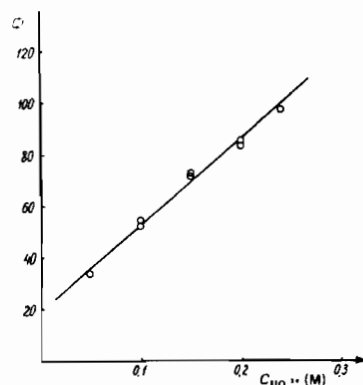


Fig. 3. Dependence of Φ on UO₂(ClO₄)₂ concentration (C(HClO₄) = 1 M).

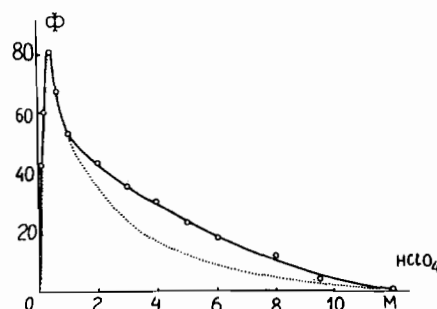


Fig. 4. Dependence of Φ on HClO₄ concentration (C_U = 0.1 M). - - -, experimental; ·····, calculated.

0.1 M. Here the exchange proceeds as a bioxygen process in the 0.4–12 M HClO₄ region; as a monooxygen process in the ≤0.03 M HClO₄ region; and as a mixed process in the 0.03–0.4 M HClO₄ region. Quantum yields of mono (Φ_1) and bioxygen (Φ_2) mechanisms of exchange in the region 0.01–0.4 M HClO₄ are given in Table II. Up to 0.4 M HClO₄ Φ rapidly increases and roughly $\Phi_1 \sim [H^+]$ and $\Phi_2 \sim [H^+]^2$. Further increase in the acidity leads to diminishing values of Φ .

Results and Discussion

Nature of the Exchange Centre

The 'chemical' arguments were used here to discover the constitution of the exchange centre. Let us introduce into the uranyl-containing solution a sort

TABLE II. Quantum Yield of Photostimulated Oxygen Exchange of Uranyl at Low Concentration HClO₄ Region

pH	C(HClO ₄) (M)	Φ	Φ ₁	Φ ₂
0.4	0.4	80 ± 5	5 ± 5	75 ± 3
0.7	0.2	61 ± 5	18 ± 5	43 ± 3
1.0	0.1	43 ± 4	33 ± 4	10 ± 2
1.2	0.06	17 ± 3	15 ± 2	2 ± 2
1.5	0.03	8 ± 1	8 ± 1	0 ± 1
2.0	0.01	3 ± 1	3 ± 1	0 ± 1

$C_U = 0.1 \text{ M}; I = 1.2 \times 10^5 \text{ E l}^{-1} \text{ s}^{-1}; 25 \text{ }^\circ\text{C}.$

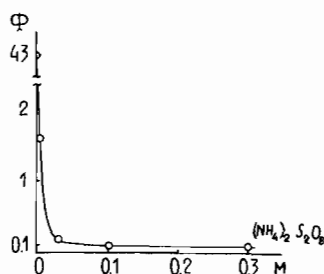
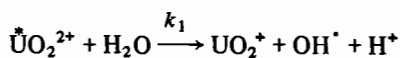


Fig. 5. Dependence of Φ on (NH₄)₂S₂O₈ concentration ($C_U = 0.1 \text{ M}, C(\text{HClO}_4) = 0.1 \text{ M}.$)

of oxidizing agent which does not quench the uranyl luminescence (luminescence yield is proportional to the concentration of long-lived excited uranyl state, UO_2^{2+}). This additive would not change the oxygen exchange rate if the catalyst is the excited uranyl but would diminish it if the catalyst is the reduced uranyl form. Peroxo-disulphate ion was used as such an oxidizing agent. Indeed, the addition of the $\text{S}_2\text{O}_8^{2-}$ ion quenches the uranyl luminescence yield to a very small extent (less than 10%). The $\text{S}_2\text{O}_8^{2-}$ ion is also a weak complexing agent and does not absorb in the visible region of the spectrum.

Figure 5 shows that Φ is steeply diminished with an increase in the peroxo-disulphate concentration and reaches the limit $\Phi = 0.08$ at $C[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.03 \text{ M}$. Thus the experiment with peroxo-disulphate solves the alternative in favour of the point of view that it is the reduced form of uranyl which catalyses oxygen exchange.

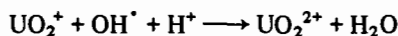
In the perchlorate solutions the only real photochemical process which leads to reduced uranyl form formation is the reaction:



with uranoyl ion exchanging its oxygen atoms rapidly with water molecules and its electrons with uranyl ion. In this case the limit $\Phi = 0.08$ can be considered as the quantum yield of the primary exchange – the process in which uranoyl ion generated by light has time to exchange its oxygen atoms but does not have

time to exchange an electron before ruin, and to give rise to an exchange chain.

We found that the oxygen exchange processes generated by light and addition of Eu^{2+} , which is known to reduce rapidly uranyl to uranoyl, have similar characteristics. There are differences in the exchange kinetics and they show a greater UO_2^+ destruction speed in the case of photostimulated exchange. This is explained by the faster kinetics of the recombination reaction:



in comparison with the UO_2^+ disproportionation reaction.

Action of Reagents

Reagent influence is determined by its action on the uranoyl (oxidation), on the uranyl (complexation) or on the photoexcited uranyl (reduction). Bubbling gaseous chlorine through the irradiated solution of uranyl perchlorate diminishes Φ to 0.07, oxygen to 10, oxygen and ozone (~4 vol.%) mixture to 1.2. Helium deaeration of these solutions reduces Φ as much as its initial value, 53. Similarly the thermal decomposition of peroxo-disulphate in solution by heating at 80 °C also reduces the initial Φ value. These experiments show that the uranyl solutions do not contain low oxidation state uranium before the light irradiation.

The examined cations can be divided into three groups.

(i) Inactive cations

In accordance with their redox potentials these cations cannot change the valence state of UO_2^{2+} or UO_2^+ . They are Mg(II), La(III) and Th(IV). All these cations slowly reduce Φ values. The dependence of Φ on the cation concentration is satisfactorily described by the equation:

$$\Phi_0/\Phi = 1 + K\sqrt{C_M}$$

Here Φ_0 = quantum yield without cation, Φ = quantum yield with cation, K = constant, C_M = cation concentration.

Figure 6 shows Φ vs. C_M dependence of coordinates Φ_0/Φ vs. $\sqrt{C_M}$. The increase in the straight line slope takes place as the cation charge is increased.

The idea of cation–cation complex [$\text{UO}_2^+ \cdot \text{M}^{n+}$] formation satisfactorily agrees with such a dependence if the bonded uranoyl recombines with hydroxyl radical faster than free UO_2^+ . Probably complexation facilitates recombination, removing orientation difficulties [10].

(ii) Cation-oxidizers of uranoyl: Fe(III) and Ag(I)

The addition of salts of these metals sharply diminishes Φ (see Fig. 7). But the Fe(II) formed is an effective reductant of the excited uranyl. As the real

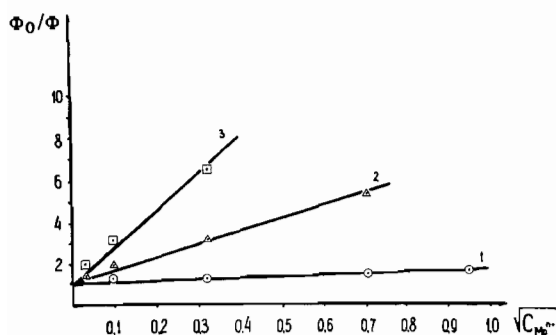


Fig. 6. Dependence of Φ on 'inactive' cation concentration ($C_U = 0.1$ M, $C(\text{HClO}_4) = 1$ M).

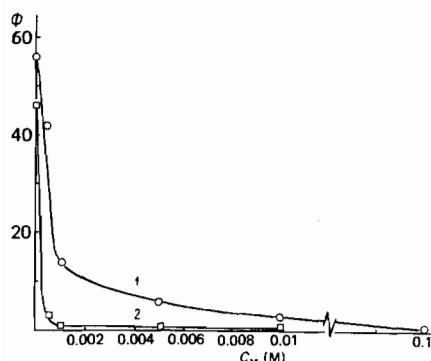
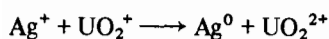


Fig. 7. Dependence of Φ on concentration of cation-oxidizers of UO_2^{2+} ($C_U = 0.1$ M, $C(\text{HClO}_4) = 1$ M): (1) Ag(I); (2) Fe(III).

Fe(II) concentration is small ($\sim 10^{-6}$ M) the reverse reaction of UO_2^{2+} reduction is not considerable and the equilibrium is at $\Phi = 0.9$.

The black deposit of Ag metal (as identified by emission analysis) was found in the irradiated solutions to contain Ag^+ . Its probable formation reaction is:



(iii) Cations Mn(II), Ce(III) and Fe(II)

These can be classified as reductants of the excited uranyl because as a whole their introduction leads to an increase in Φ (see Fig. 8), i.e. an increase in UO_2^+ concentration. In the case of M^{n+} (weak reductants) the curves have a minimum in the low M^{n+} concentration region. This minimum probably is due to the general form of the cations' function of recombination centre of $\text{UO}_2^+ + \text{OH}^+$ reaction, which diminishes Φ . In the case of Fe(II) the curve has no minimum. The plateau of curves in Fig. 8 is the result of an equilibrium between oxidation of UO_2^+ by an oxidized cation form and reduction of UO_2^{2+} by the initial cation form.

As with the cations, anions can also reduce photoexcited uranyl or oxidize uranyl and affect the

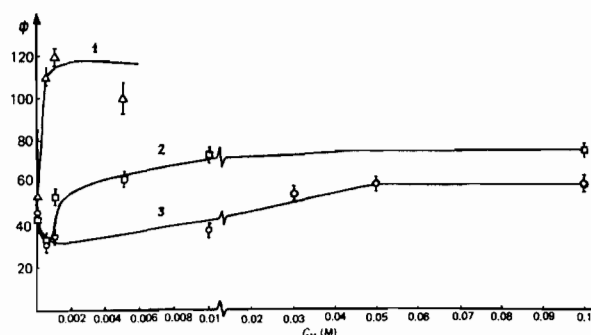


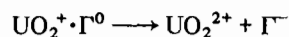
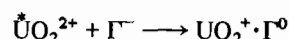
Fig. 8. Dependence of Φ on concentration of cation-reductants of UO_2^{2+} ($C_U = 0.1$ M, $C(\text{HClO}_4) = 1$ M): (1) Fe(II), (2) Ce(III), (3) Mn(II).

TABLE III. Dependence of Φ on Concentration of Anion Added^a

Anion	Anion conc. (M)	Φ
NO_3^-	0.01	56 ± 5
	0.1	50 ± 5
SO_4^{2-}	0.01	56 ± 5
	0.1	42 ± 4
Br^-	0.01	52 ± 5
	0.1	14 ± 2
Cl^-	0.01	11 ± 2
	0.1	53 ± 5
	0.01	5 ± 1
	0.1	2 ± 1

^a $C(\text{HClO}_4) = 1$ M, $C_U = 0.1$ M.

photostimulated oxygen exchange of uranyl. But in contrast to cations they can form complexes with uranyl and reduce exchange at the stage of electron exchange U(V)–U(VI). The results are shown in Tables III and IV. Nitrate and sulphate (weak complexing agents) insignificantly affect Φ values. Cl^- and Br^- are weak complexing agents too, but they lower Φ significantly. We may suppose that the action of Γ^- ($\Gamma = \text{Cl}, \text{Br}$) is determined by the reversible electron transfer on UO_2^{2+} . For a time of Γ^0 localization in the coordination sphere of UO_2^+ , the reverse reaction is more or less completed:



Acetate ion acts as a typical complexing agent. The acetate concentration growth lowers Φ . Carbonate, which is a strong complexing agent and also a quencher of the excited uranyl state, completely stops the exchange.

TABLE IV. Dependence of Φ on Concentration of Strong Complexing Agents

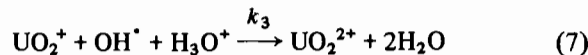
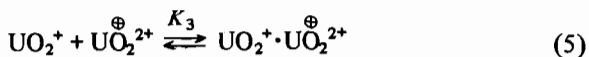
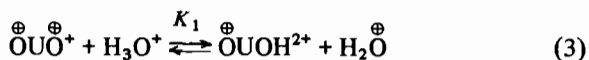
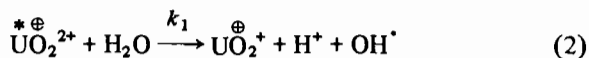
Initial complex	Free anion conc. (M)	C_U (M)	Φ	Half exchange time in dark (h)
CsUO ₂ (CH ₃ COO) ₃	0.55		4	3.25
	1.65	0.05	0.5	51
	4.05			115
RbUO ₂ (CO ₃) ₃	0.1		exchange is not found	
	0.58			
	1.05	0.1		
	1.68			
	2.6			

Exchange Mechanism

The tendency of Φ to vanish at vanishing HClO₄ concentrations shows that the oxygen exchange is realised by protonated forms of uranyl. The formation of these forms is possible due to electron-donor or proton-acceptor function of uranyl oxygen atoms [11, 12]. We may suppose that the monooxygen exchange takes place at the monoprotonated form (OUO·H²⁺) and bioxygen exchange at the biprotonated form (H·OUOH³⁺) or uranyl formation (see Table II).

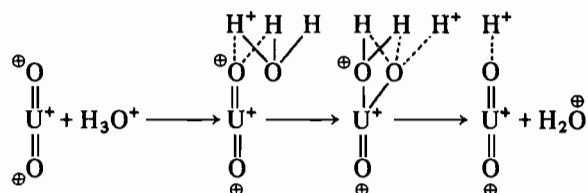
The Φ increase from $\Phi_H = 53 \pm 5$ to $\Phi_D = 78 \pm 8$ on the substitution of H by D ($C(\text{DClO}_4) = 1 \text{ M}$, $C_U = 0.1 \text{ M}$) in solution takes place. The positive effect of deuterio substitution is evidence for the establishment of the acid-base equilibrium in the system. Therefore protonated form formation is not the slow, rate-determining stage of the process [13, 14].

Taking into account the foregoing experiments, we can represent the photostimulated oxygen exchange by the following system of subsequent reactions (* = excited state, \oplus = isotope mark):



The first reaction describes the light absorption by uranyl, the second, water oxidation by photoexcited uranyl. Reactions (3) and (4) symbolize the formation of uranyl mono- and biprotonated forms. This formation is accompanied by oxygen exchange with the hydroxonium ion. It can be supposed that the rate of biprotonated uranyl formation is greater than the rate of monoprotonated form dissociation. Then the subsequent oxygen exchange would be perceived as synchronous bioxygen exchange.

The most probable form of transitional complex in which oxygen exchange takes place is thus:



Reactions (5) and (6) describe electron exchange between uranyl and uranyl ions – the process that is responsible for the oxygen exchange ‘reproduction’. Finally reaction (7) shows the end of the oxygen exchange chain – recombination.

We see that reactions (3), (4) and (7) determine the decrease in oxygen exchange rate with increase in solution acidity.

On the basis of the obtained experimental data an estimation of the constant values was carried out: $k_1 = (4.35 \pm 0.1) \times 10^4 \text{ s}^{-1}$; $k_2 = (1.0 \pm 0.1) \times 10^3 \text{ s}^{-1}$; $k_3 = (1.5 \pm 0.2) \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$; $K_1 = (1.5 \pm 0.1) \text{ l mol}^{-1}$; $K_2 = (5 \pm 0.5) \text{ l mol}^{-1}$; $K_3 = (25 \pm 5) \text{ l mol}^{-1}$.

The whole set of these constants roughly describes the experimental dependence of Φ on $C(\text{HClO}_4)$ (the calculated curve is dotted in Fig. 3).

Influence of Light Intensity

In accordance with the represented scheme of photostimulated oxygen exchange, the rate of uranyl formation is proportional to the first power of the absorbed light intensity, I (reactions 1 and 2) and rate of disappearance to the second power (reaction 7). This gives the following dependence:

$$\Phi \sim 1/\sqrt{I}$$

But from data from ref. 5, Φ is independent of I . We have undertaken experimental verification of the Φ vs. I dependence because the conclusion of ref. 5 was made on the basis of a small number of experimental values and a narrow interval of variation in I .

TABLE V. Dependence of Φ on Absorbed Light Intensity at Impulse Irradiation^a

I (quant. imp. ⁻¹ ml ⁻¹ $\times 10^{-16}$)	Φ	I^0/I	$\sqrt{(I^0/I)}$	$\Phi^0\sqrt{(I^0/I)}$
Series No. 1				
3.42 (I^0)	82 ± 4 (Φ^0)	1	1	82
0.44	243 ± 15	7.94	2.81	230
0.28	275 ± 20	12.27	3.5	287
Series No. 2				
3.42 (I^0)	86 ± 4 (Φ^0)	1	1	86
1.64	140 ± 8	2.07	1.44	124
0.89	186 ± 10	4	2	172
0.44	254 ± 15	8	2.83	243

^a $C_U = 0.1$ M, $C(\text{HClO}_4) = 1$ M, 25 °C; $\lambda_{\text{max}} = 400$ nm.

TABLE VI. Dependence of Φ on Absorbed Light Intensity at Continuous Irradiation^a

I ($\text{E } \Gamma^{-1} \text{ s}^{-1} \times 10^6$)	Φ	I^0/I	$\sqrt{(I^0/I)}$	$\Phi^0\sqrt{(I^0/I)}$
6.9 (I^0)	86 ± 4 (Φ^0)	1	1	86
3.45	128 ± 6	2	1.41	121
1.72	170 ± 10	4	2	172
0.86	260 ± 15	8	2.83	243

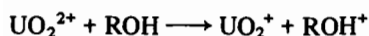
^a $C_U = 0.1$ M, $C(\text{HClO}_4) = 1$ M, 25 °C; $\lambda_{\text{max}} = 436$ nm.

Our data, which were obtained at continuous and at impulse light irradiation, definitely show that $\Phi \sim 1/\sqrt{I}$ (see Tables V and VI). This circumstance is a strong additional argument in favour of our scheme of uranyl photostimulated oxygen exchange.

Oxygen Exchange and Photochemical Properties of Uranyl Ions

The foregoing data show that the determination of oxygen exchange mechanism and kinetics can be an effective method for the investigation of redox and photochemical reactions with uranyl and probably other actinyl ion participation, because these reactions usually proceed through unstable intermediate oxidation forms. The oxygen exchange allows one to discover very low uranyl concentrations owing to long chains of uranyl–uranoyl electron exchange (hundreds and thousands of links) and irreversible transition of oxygen-18 from uranyl to water.

For instance, let us consider photooxidation of alcohols by uranyl ion. The traditional view of uranyl formation at the first stage of photochemical process is:



This agrees poorly with a quantum yield 0.7 for U(IV). The latter value has been obtained in one of

the experiments with a water–ethanol system [15]. This $\Phi_{\text{U(IV)}}$ value exceeds the highest limit (0.5) for the mentioned mechanism. An attempt was made [15] to explain this by the accompanying reaction of photochemical reduction of UO_2^+ by ethanol. But the experimental verification of this idea did not give a definite result.

A value $\Phi_{\text{U(IV)}} > 0.5$ was also found with the uranyl fluoride photoreduction in methanolic solution (water content 1.1 M) [16]. Here the oxygen exchange between uranyl and water was not found. On this basis, it was supposed [16] that the uranyl photoreduction was realized by the transfer of two electrons to UO_2^{2+} from the methanol molecule.

We investigated oxygen exchange of uranyl in irradiated dilute ethanol solutions. The results are shown in Fig. 9. Both the high Φ values and the curve form with the plateau prove at least partial formation of uranyl ion at the first step of the photochemical process. In addition, the determination of U(IV) quantum yield gave $\Phi_{\text{U(IV)}} = 0.51 \pm 0.05$ at an ethanol concentration of 0.2 M. Thus the main initial product of photochemical reduction of uranyl in dilute aqueous solutions of ethanol is uranyl.

Figure 10 shows the Φ dependence on the wavelength of irradiating light. In the case of water–ethanol solutions it has a plateau after an increase from $\lambda = 360$ nm to $\lambda = 480$ nm. A curve form characterizes the efficiency of population of the

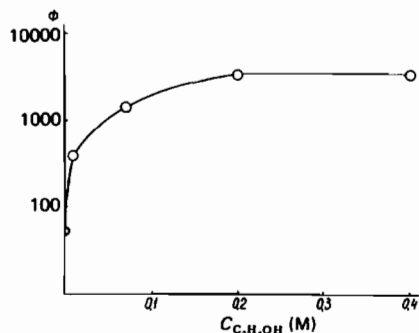


Fig. 9. Dependence of Φ on ethanol concentration ($C_U = 0.1$ M, $C(HClO_4) = 1$ M).

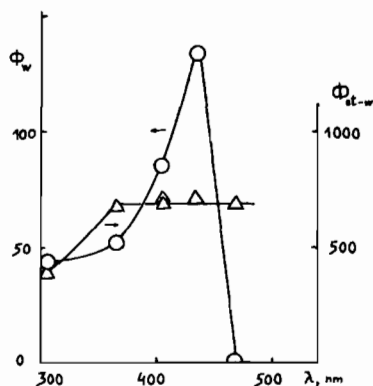


Fig. 10. Dependence of Φ on light wavelength ($C_U = 0.1$ M): (1) water, $C(HClO_4) = 1$ M; (2) ethanol-water mixture, $C(\text{ethanol}) = 0.4$ M, $C(HClO_4) = 4$ M.

photochemically active levels at absorption of light with different wavelengths, the latter ones lie at $\lambda \geq 400$ nm for ethanol molecules.

The analogous dependence for aqueous solutions has a pronounced maximum at 440 nm. The photon energy 2.82 eV corresponds to this maximum (it is interesting that this energy value coincides with the value of water oxidation potential [17]). Rapidly vanishing Φ values already at $\lambda = 470$ nm show that this energy is near to the threshold of the reaction of water oxidation by photoexcited uranyl.

Conclusions

Being a characteristic of photochemical channel of uranyl deactivation, the oxygen exchange (in com-

bination with luminescence) allows one to obtain more complete knowledge about the complex process of photoexcited uranyl deactivation. In a more general sense the oxygen exchange can be used for the discovery of particles with the lowered bond order of the metal-oxygen bond in the different reactions of actinyl ions. It is interesting that a strong acceleration of neptunyl oxygen exchange takes place under the action of ozone and cerium(IV), while $KMnO_4$ and other less strong oxidizers retard exchange [18]. Probably this is related to the formation of unstable $Np(VII)$ forms, which have lower $Np-O$ bond order than neptunyl.

Rapid and non-photosensitive monooxygen exchange of uranyl in the $pH = 3$ region is apparently caused by hydrolyzed uranyl forms arising with considerably lower $U-O$ bond order.

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