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Chemiluminescence by the interaction of XeO_3 and the products of photolysis of uranyl solutions in sulfuric acid

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Using the chemiluminescence oxidation of U(IV) and H_2O_2 with xenon trioxide as a model, it has been found that during the photolysis of solutions of UO_2SO_4 in sulfuric acid in the absence of any organic compounds, the accumulation of $U(SO_4)_2$ and H_2O_2 takes place as a result of the reaction of the primary products of the photoreduction of uranyl ion, *i.e.*, UO_2^+ and the $\cdot OH$ radical.

Key words: uranyl, xenon trioxide, hydrogen peroxide, photolysis, chemiluminescence.

The decomposition of organic compounds in the presence of uranyl salts irradiated by light have been known for more than hundred years.[1] The detachment of the hydrogen atom (or electron) from a donor SH_2 is the main photochemical reaction of the uranyl ion (UO_2^{2+}):

$$^*UO_2^{2+} + SH_2 \rightarrow UO_2^+ + {}^\cdot SH + H^+, \quad (1)$$

Taking into account the high oxidation potential (E^0 = 2.7 V) of the electron-excited uranyl ion, it was assumed[2] that photoreduction of UO_2^{2+} can also occur in the absence of organic compounds in an aqueous solution:

$$^*UO_2^{2+} + H_2O \rightarrow UO_2^+ + {}^\cdot OH + H^+, \quad (2)$$

$$^\cdot OH + {}^\cdot OH \rightarrow H_2O_2, \quad (3)$$

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

It has also been suggested that some portion of the UO_2^{2+} ions and $^\cdot OH$ radicals leave the cage and participate in reactions (3) and (4) to form the U(IV) and H_2O_2 accumulating in the solutions. However, direct proof of the validity of the photoreduction mechanism of UO_2^{2+} by H_2O has not yet been found.[3]

We attempted for the first time to study the photolysis of UO_2^{2+} in aqueous solutions of H_2SO_4 (0.2—1.0 *M*) using chemiluminescent (CL) methods based on the possibility of determining small amounts (~ 10^{-9} mol/L) of uranium(IV) on the background of a great excess (~10^{-1} mol/L) of UO_2^{2+} by means of the CL oxidation of uranium(IV) with xenon trioxide.[4]

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Experimental

A SDV-120 medium pressure mercury lamp was used as the light source. The spectral range with $\lambda \geq 400$ nm was separated out with light filters (the absorption maximum of UO_2SO_4 lies in the range from 400 to 500 nm, see Ref. 1). Chemiluminescence was registered by a photometric setup, whose sensitivity in the blue spectral range reaches 10^3 photons/(s cm^3) with the use a FEU-140 photomultiplier. Chemically pure grade sulfuric acid twice distilled till the absence of absorption in the UV spectral range ($\lambda \geq 200$ nm) in a 5 cm cuvette was used for the preparation of dilute aqueous solutions of H_2SO_4. The acid concentration was controlled by potentiometric titration. Hydrogen peroxide was prepared according to the known procedure.[3] The solutions of the uranium(IV) salts were prepared by the electrolytic reduction of the uranyl solutions in 1 *M* H_2SO_4 on a platinum electrode in an electrolyzer with separated anodic and cathodic areas. The solutions of XeO_3 were obtained by dissolving of a weighed sample of $Na_4XeO_6{\cdot}6H_2O$ in the acid. The concentration of XeO_3 was determined by iodometric titration.[6]

All solutions were prepared with bidistilled water. The reaction rate constant of the oxidation of U(IV) by xenon trioxide was determined in a great excess of the oxidant (under conditions when this reaction follows a pseudo-first order kinetic equation).

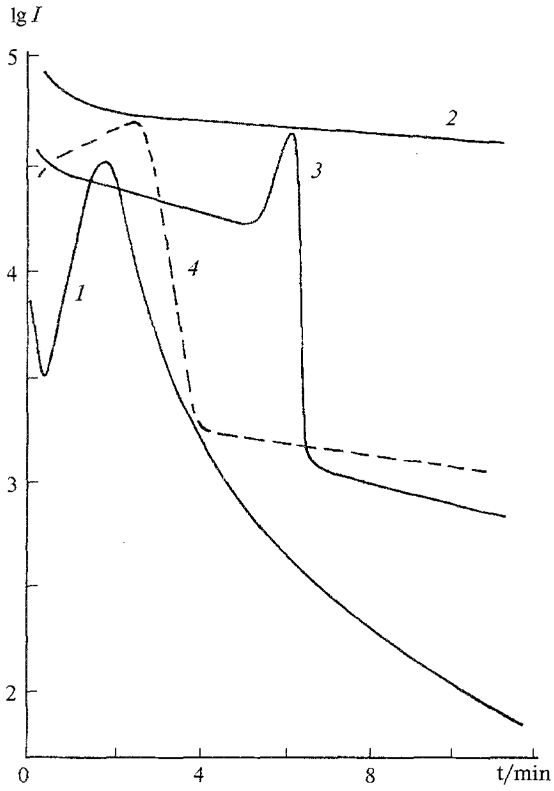

Fig. 1. Kinetics of the chemiluminescence that accompanies the interaction of XeO_3 with the photolysis products $UO_2{}^{2+}$ in 0.2 *M* H_2SO_4 (*1*); $U(SO_4)_2$ (*2*); $U(SO_4)_2 + H_2O_2$ (*3*); $U(SO_4)_2 + UO_2SO_4 + H_2O_2$ (*4*).
$[UO_2{}^{2+}] = 10^{-2}$; $[XeO_3] = 10^{-4}$; $[U(IV)] = 2.5{\cdot}10^{-5}$; $[H_2O_2] = 2.5{\cdot}10^{-4}$ mol/L, $T = 293$ K, 1 *M* H_2SO_4.

Results and Discussion

We found that mixing the XeO_3 solution with the UO_2SO_4 solution in 1 *M* H_2SO_4 preliminarily irradiated with the light of the SVD-120 lamp for 1 h resulted in chemiluminescence, whose intensity reached 10^8 photons/(s cm^3). The CL spectrum coincides with that of the photoluminescence of $^*UO_2SO_4$ in a 1 *M* solution of H_2SO_4. The kinetics of CL is determined by a curve with a maximum (Fig. 1, curve *1*).

It is known[4] that in an excess of an oxidant the CL intensity that accompanies reaction (5) decreases exponentially with time (Fig. 1, curve *2*).

$$\mathrm{XeO_3 + 3\,U^{4+} + 3\,H_2O} \begin{array}{l} \longrightarrow \mathrm{2\,UO_2^{2+} + Xe + 6\,H^+} \\ \searrow \overset{*}{\mathrm{U}}\mathrm{O_2^{2+}} \longrightarrow \mathrm{UO_2^{2+}} + h\nu . \end{array} \qquad (5)$$

The existence of the maximum on the curve *1* (Fig. 1) means that the luminescence that accompanies the interaction between XeO_3 and the photolysis products of the UO_2SO_4 solution is not exhausted by the CL-reaction of the oxidation of U(IV) by xenon trioxide.

We have shown previously[7] that in the presence of H_2O_2, reaction (5) does not correspond to first-order kinetics (Fig. 1, curve *3*). The existence of a maximum, which is formed a certain time interval after the beginning of the reaction in the U(IV)—XeO_3—H_2O_2 system, is a characteristic feature of the kinetic curve. The time dependence of the CL intensity characterized by the existence of an induction period and a pronounced maximum is realized only in a narrow concentration range of U(IV) (at fixed XeO_3 and H_2O_2 concentrations; Fig. 2, curve *2*). Both at higher and lower amounts of U(IV) in the solution (Fig. 2, curves *1* and *3*, *4*, respectively), the kinetics of the CL-stage of the oxidation of U(IV) by the products of the interaction between H_2O_2 and XeO_3 is determined by monotonic curves.[7]

We believe that the processes occurring in an aqueous solution of H_2SO_4 containing $U(SO_4)_2$, UO_2SO_4, XeO_3, and H_2O_2, have a radical-chain mechanism. The chain may be initiated by the reactions:

$$\mathrm{U(IV) + XeO_3 + H_2O} \xrightarrow{k_6} \mathrm{U(V) + XeO_2 + \dot{O}H + OH^-}, \qquad (6)$$

$k_6 = 33$ mol^{-1}s^{-1}

$$\mathrm{U(IV) + H_2O_2} \xrightarrow{k_7} \mathrm{U(V) + \dot{O}H + OH^-}, \qquad (7)$$

$k_7 = 1.6$ mol^{-1}s^{-1}

$$\mathrm{H_2O_2 + XeO_3} \xrightarrow{k_8} \mathrm{XeO_2 + \dot{O}H + OH^-}, \qquad (8)$$

$k_8 > 1$ mol^{-1}s^{-1}

The presence of a maximum on the kinetic curve can be explained by assuming that the interaction of XeO_3 with H_2O_2 has an autocatalytic character. For the first

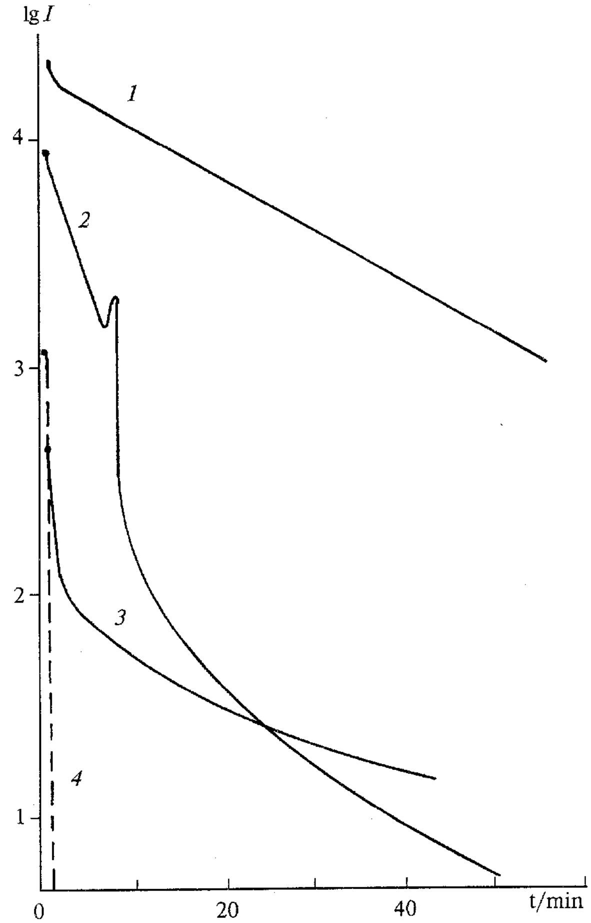

Fig. 2. Time dependence of the intensity of the luminescence emitted from a 1 *M* H_2SO_4 solution containing $U(SO_4)_2$, XeO_3, and H_2O_2 with different U(IV) concentrations, mol/L: $8\cdot10^{-5}$ (*1*); $2\cdot10^{-5}$ (*2*); $4\cdot10^{-6}$ (*3*); $4\cdot10^{-7}$ (*4*).
$T = 293$ K. $[XeO_3] = 4\cdot10^{-5}$; $[H_2O_2] = 2.5\cdot10^{-4}$ mol/L.

few minutes after the solutions of U(IV), XeO_3, and H_2O_2 have been mixed, when the U(IV) concentration is still rather high, a significant portion of the ·OH radicals formed in reactions (6)—(8) rapidly decays, predominantly by interaction with U(IV) and U(V) according to reactions (9) and (10):[8]

$$U(IV) + \dot{O}H \xrightarrow{k_9} U(V) + OH^-, \qquad (9)$$

$$k_9 = 8\ 10^8\ mol^{-1}s^{-1}$$

$$UO_2^{\ +} + \dot{O}H \xrightarrow{k_{10}} \overset{*}{U}O_2^{2+} + OH^-, \qquad (10)$$

$$k_{10} > 10^9\ mol^{-1}s^{-1}$$

Therefore, there is no autoacceleration of reaction (8). It should be mentioned that CL of the uranyl ion can be observed not only in reaction (10), but also in the oxidation of U(V) by hydrogen peroxide or xenon trioxide, however, the rate constants of these processes are lower than that of reaction (10) by several orders of magnitude.[9]

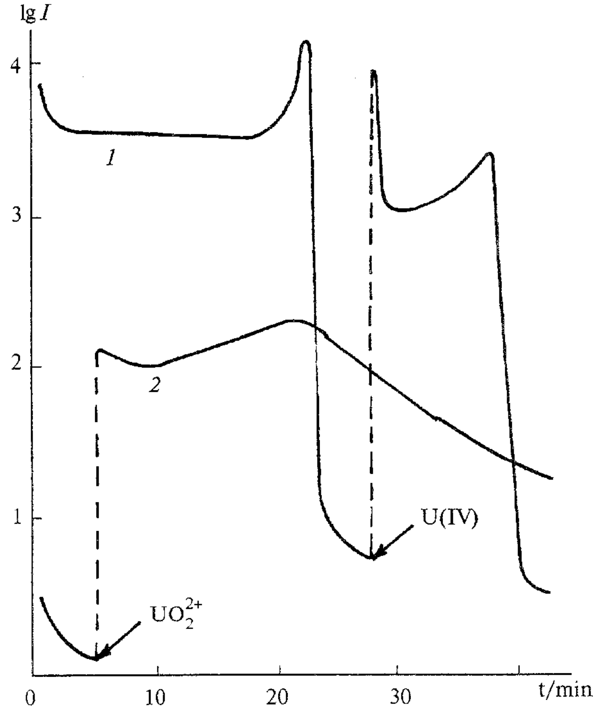

Fig. 3. Chemiluminescence kinetics in the interaction of $U(SO_4)_2$, XeO_3, and H_2O_2 before and after introduction of $2.2\cdot10^{-5}$ mol/L of $U(SO_4)_2$ in 1 *M* H_2SO_4 (*1*); XeO_3 and H_2O_2 before and after introduction of $9\cdot10^{-3}$ mol/L of UO_2^{2+} into the solution (*2*). $T = 276$ K; $[U(IV)] = 2.5\cdot10^{-5}$; $[H_2O_2] = 2.5\cdot10^{-4}$; $[XeO_3] = 10^{-4}$ mol/L.

The kinetics of CL in the solution containing U(IV), XeO_3, and H_2O_2 differs at the initial stage from the kinetics of reaction (5) only in a more abrupt drop in the luminescence intensity due to the consumption of U(IV) in the reaction with hydrogen peroxide (Fig. 1, curves *2* and *3*). The fraction of ·OH radicals interacting with XeO_3 and H_2O_2 increases with the decrease in $U(SO_4)_2$ in the solution due to reactions (6), (7), and (9). This, in its turn, increases the ·OH concentration in the solution and, hence, the oxidation rate of U(IV) and U(V). Under appropriate conditions, the process becomes avalanche-like, and the CL intensity increases rapidly and reaches the maximum at the moment when the rate of the generation of ·OH radicals exceeds that of the formation of U(V) by the oxidation of U(IV). The repeated introduction of $U(SO_4)_2$ into the solution can reproduce the kinetic curve with the induction period, autoacceleration, and the abrupt drop in the CL intensity after passing the luminescence peak (Fig. 3, curve *1*; the moment of the repeated introduction of U(IV) into the solution is indicated by the point).

The interaction between H_2O_2 and XeO_3 is accompanied by weak CL, whose intensity increases in the presence of uranyl ions.[10] The fact that the kinetic curve has a maximum, which is characteristic of autocatalytic reactions and is obtained for the oxidation of H_2O_2 with xenon trioxide in 1 *M* H_2SO_4 (Fig. 3, curve *2*), and the good time correlation of curves *1* and *2* (curve *3*) attest to the validity of the assumptions made for explaining kinetic peculiarities of the CL-process observed in the interaction of U(IV), XeO_3, and H_2O_2 in aqueous solutions of sulfuric acid.

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Synthesis of diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines

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A series of previously unknown diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines was prepared by the reaction of diphenyl(trimethylsilyl)phosphine with carbonyl compounds. The first complexes of these ligands with palladium chloride were prepared.

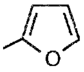
Key words: diphenyl(trimethylsilyl)phosphine, reactions with aldehydes and ketones.

It is known that functionally substituted tertiary phosphines behave as ligands of transition-metal complexes.[1] In the present work a general synthesis of diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines has been proposed and complexes of these compounds with palladium chloride have been prepared.

It is known that diethyl(trimethylsilyl)phosphine reacts with formaldehyde to produce diethyl(trimethylsilylmethyl)phosphine[2] and with α,β-unsaturated aldehydes to give products of 1,4-addition .[2,3]

We have found that less active diphenyl(trimethylsilyl)phosphine (**1**) reacts with some aliphatic and aromatic aldehydes at room temperature to produce the corresponding diphenyl[alkyl(aryl)trimethylsiloxymethyl]phosphines (**2a**—**e**). Phosphine yields are 50—70 %.

$$\underset{\mathbf{1}}{Ph_2P{-}SiMe_3} + R{-}CHO \xrightarrow[3\,h]{20^\circ C} \underset{\mathbf{2a{-}e}}{Ph_2PCH(R)OSiMe_3}$$

R = Et(**a**), Pr(**b**), *i*-Pr(**c**), Ph(**d**),  (**e**).