Uranyl-catalyzed chemiluminescent reaction of U^{4+} oxidation by dioxygen in aqueous $HClO_4$ solution

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Chemiluminescence (CL) accompanying the reaction of U^{4+} with O_2 in 0.0004—0.1 *M* $HClO_4$ was studied. It was found that the electron-excited uranyl ion $(UO_2^{2+})^*$ is the CL emitter. The fact that the reaction rate and the CL yield increase as the solution acidity decreases was explained by different reactivities of the U_{aq}^{4+} aquaion and the products of its stepwise hydrolysis, UOH^{3+} and $U(OH)_2^{2+}$, toward O_2. Based on the results of analysis of the chain-radical mechanism of the reaction between U^{4+} and O_2, it was concluded that transfer of an electron from the UO_2^+ ion to the oxidizing agent (a $^{\bullet}OH$ radical) is the most plausible elementary step of the reaction of $(UO_2^{2+})^*$ formation. It was found that the reaction rate, as well as the CL yield, increase substantially in the presence of uranyl ion. Catalytic action of UO_2^{2+} was explained by the formation of a $UO_2^{2+} \cdot UO_2^+$ complex, which reduces the rate of the UO_2^+ disproportionation reaction (UO_2^+ is an intermediate of the reaction and is involved in chain propagation), and by regeneration of the active center, UO_2^+, in the reaction of UO_2^{2+} with U^{4+}.

Key words: uranium(IV), uranyl ion (UO_2^{2+}), complex, dioxygen, kinetics, catalysis, chemiluminescence, oxidation.

Only a few of the known redox reactions of uranium compounds[1,2] are accompanied by bright chemiluminescence (CL). Light emission occurs when uranium(IV) reacts with oxidizing agents, *e.g.*, O_3,[3] OF_2,[4] H_2O_2,[5] XeO_3,[6—8] XeF_2,[9,10] and HSO_5^-.[11,12] It is of interest to clarify the questions of how the CL emitter (electron-excited uranyl ion, $(UO_2^{2+})^*$) is formed and of which factors and to what extent they affect the efficiency of conversion of the energy of chemical reaction to luminous energy. Among these factors first of all are the nature of both the oxidizing agent and solvent, the pH value of the medium, complexation, and chemical quenching of the CL emitter. In this connection, the oxidation of U^{4+} by dioxygen attracted considerable interest, since it proceeds in any non-deaerated solutions, as well as in those cases where O_2 is formed in the reactions of U^{4+} with other oxidizing agents. Our previous attempts to detect light emission from 1—5 *M* H_2SO_4 solutions containing U^{4+} and O_2 have failed. Only on going to perchloric acid solutions ($[HClO_4] \le 0.1$ mol L^{-1}) was the sensitivity of our photometric installation high enough for the recording of CL. In this work, we studied the effect of solution acidity and the uranyl ion on the kinetics of oxidation of U^{4+} by dioxygen and on the parameters of chemiluminescence accompanying this reaction.

Experimental

Equipment for the recording of CL as well as procedures for the syntheses and purification of compounds used in the experiments and preparation of solutions have been described previously.[11,12] The initial concentration of U^{4+} in the solutions under study was ~10^{-5} mol L^{-1}, which provided a 10-fold excess of the oxidizing agent (dioxygen). A solution of volume 10 mL was placed in a glass or Teflon reactor of internal diameter 38 mm, which provided efficient stirring of the solution and maintained the desired temperature with an accuracy of ±0.1 K. In the course of reaction the temperature of the solution was continuously monitored by a copper-constantan thermocouple sealed in a thin-walled glass capillary. In the range from 285 to 298 K, variations of the temperature of the solution stirred in the reactor did not exceed ±0.03 K. The accuracy of thermostatting at $T = 310$ K was ±0.05 K. The CL spectrum was estimated using a set of glass cut-off light filters.

Results and Discussion

The fact that the CL and photoluminescence of the uranyl ion are observed in the same spectral region indicates that the electron-excited $(UO_2^{2+})^*$ ion is the CL emitter.

The rate of the reaction of U^{4+} with O_2 is described by the following kinetic equation[2]:

$$-d[U^{4+}]/dt = k \cdot [U^{4+}] \cdot [O_2] \cdot [H^+]^{-1}.$$

If this also holds for the rate of the light stage of the reaction, then, under conditions of excess oxidizing agent and constant acidity of the solution, the time profile of the CL intensity should be described by the exponent

$$I_{CL} = \eta_{CL} \cdot k \cdot [U^{4+}]_0 \exp(-kt),$$

where η_{CL} is the CL yield and $[U^{4+}]_0$ is the initial U^{4+} concentration.

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It is this exponential luminescence decay that was observed in the oxidation of U^{4+} by xenon trioxide[7,8] or Caro's acid ion.[12] However, the kinetics of the chemiluminescent stage of the reaction of U^{4+} with O_2 is different. The time profiles of the CL intensity found for solutions with different $HClO_4$ concentrations pass through maxima (Fig. 1), which is typical of consecutive reactions. In the process under study, the maximum CL intensity (I_{max}) and, hence, the highest rate of the formation of $(UO_2^{2+})^*$ are observed after some time (t_{max}) rather than at the beginning of the reaction, where the concentration of U^{4+} is maximum. The kinetics of the chemiluminescent stage depends strongly on the pH value of the solution. A decrease in the $HClO_4$ concentration from 10^{-2} to $4 \cdot 10^{-4}$ mol L^{-1} causes a substantial acceleration of the reaction. The I_{max} value increases by a factor of 110 and reaches $3.7 \cdot 10^8$ photon s^{-1} and t_{max} is shortened by a factor of 30, from 750 to 25 s (see Fig. 1, curves *1* and *6*, respectively).

We believe that the effect of pH value of the medium on both the reaction kinetics and the CL parameters is due to changes in the type of U^{4+} complex involved in oxidation. It is known[2] that a stepwise hydrolysis of the U_{aq}^{4+} aquaion proceeds as the solution acidity decreases. The reaction results in the hydroxo forms UOH^{3+} and $U(OH)_2^{2+}$:

$$U_{aq}^{4+} + H_2O \overset{K_1}{\rightleftharpoons} UOH^{3+} + H^+, \quad (1)$$

$$UOH^{3+} + H_2O \overset{K_2}{\rightleftharpoons} U(OH)_2^{2+} + H^+. \quad (2)$$

The dependences of the concentrations of U_{aq}^{4+}, UOH^{3+}, and $U(OH)_2^{2+}$ ions on the pH value of the solution, obtained with $K_1 = 0.027$ and $K_2 = 1.6 \cdot 10^{-4}$,[2] are shown in Fig. 2. As can be seen, the U_{aq}^{4+} concentration decreases monotonically as the pH value increases; at the same time, the concentration of UOH^{3+} increases and reaches a maximum value near pH 2.7. Considerable amounts (1—2%) of the hydroxo form $U(OH)_2^{2+}$ appear only near the pH value of 2 (see Fig. 2, curve *3*).

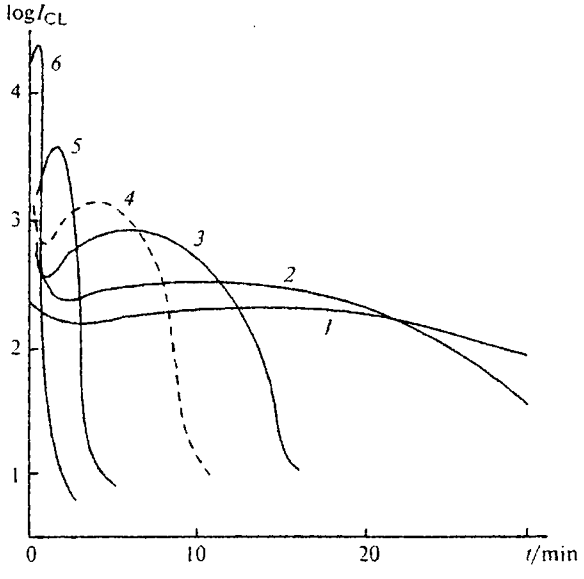

Fig. 1. Kinetic curves for chemiluminescence accompanying the reaction of U^{4+} with O_2 in air-saturated aqueous $HClO_4$ solutions at 313 K ($[U^{4+}]_0 = 10^{-5}$ mol L^{-1}): $[HClO_4]$/mol L^{-1} = 0.01 (*1*), 0.007 (*2*), 0.003 (*3*), 0.002 (*4*), 0.001 (*5*), and 0.0004 (*6*) (I_{CL} is the CL intensity).

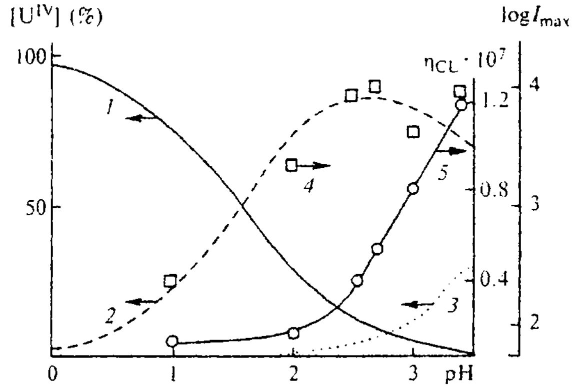

Fig. 2. Calculated concentrations of U_{aq}^{4+} aquaion (*1*) and the products of its hydrolysis, UOH^{3+} (*2*) and $U(OH)_2^{2+}$ (*3*), the CL yield (η_{CL}) (*4*), and the maximum CL intensity (I_{max}) corrected for the increase in η_{CL} (*5*) as functions of the pH value of perchloric acid solution at 313 K ($[U^{4+}]_0 = 10^{-5}$ mol L^{-1}).

It should be pointed out that the pH profiles of the CL yield and UOH^{3+} concentration for the chemiluminescent stage of the oxidation of U^{4+} by dioxygen (see Fig. 2, curves *4* and *2*, respectively) correlate well with each other. The dependence of the maximum CL intensity on pH is also shown in Fig. 2. Comparison of curve *5* with the pH profiles of the concentrations of different forms of uranium(IV) (see Fig. 2, curves *1*—*3*) suggests that the rates of the oxidation of U_{aq}^{4+}, UOH^{3+}, and $U(OH)_2^{2+}$ by dioxygen differ appreciably from one another. We failed to detect CL at 293 K and $[U^{4+}] = 10^{-3}$ mol L^{-1} in a 1 *M* $HClO_4$ solution in which most of the U^{4+} ions are present in the form of aquaions. The possibility of recording CL at 293 K and $[U^{4+}]_0 = 10^{-4}$ mol L^{-1} appears only on going to 0.1 *M* $HClO_4$ solution (pH 1) in which the concentration of UOH^{3+} ions is 25%. Here, the initial CL intensity (I_0) is $2 \cdot 10^5$ photon s^{-1} (the volume of the solution was 10 mL). Raising the temperature up to 313 K allows studying the reaction kinetics at $[U^{4+}]_0 \le 10^{-5}$ mol L^{-1}. Exponential portions of the pH profiles of I_{max} have different slopes and intersect in the pH range in which the UOH^{3+} concentration reaches a maximum value and $U(OH)_2^{2+}$ ions appear (see Fig. 2, curve *5*). An increase in I_{max} is observed at pH > 2.5, which is likely due to an increase in the $U(OH)_2^{2+}$ concentration. This suggests that the U_{aq}^{4+} aquaions are the least reactive, the reaction between the monohydroxo complex UOH^{3+} and O_2 proceeds faster, and the $U(OH)_2^{2+}$ ion exhibits the highest reactivity toward O_2.

A decrease in the CL intensity, which is observed at the beginning of the reaction, can be explained by the fact that a small amount of $U(OH)_2^{2+}$ ions and a large excess of UOH^{3+} ions are present in the 0.01 *M* $HClO_4$ solution. The fast reaction of $U(OH)_2^{2+}$ with O_2 causes CL whose intensity is greater than that of the glow due to the oxidation of UOH^{3+}. The I_0 value increases and the decay time of the initial portion of the kinetic curve is shortened as pH increases, so that the reaction of $U(OH)_2^{2+}$ with O_2 makes the major contribution to the CL at pH 3 (see Fig. 1, curve *5*).

The assumption that a complex shape of the kinetic curve is due not only to the chain-radical mechanism of the reaction, but also simultaneous involvement of several forms of uranium(IV) with appreciably different reactivities toward O_2 in the redox process is indirectly confirmed by the temperature effect of the reaction kinetics. Raising the temperature of a 0.001 *M* $HClO_4$ solution containing $2.7 \cdot 10^{-5}$ mol L^{-1} of uranium(IV) from 285 to 310 K leads to a substantial (by a factor of 280) increase in I_0; simultaneously, I_{max} increases by a factor of 30 and t_{max} is shortened by a factor of 22 (Fig. 3, curves *1* and *4*, respectively). Such a great increase in I_0 can be explained by appreciable increase in the K_2 value with temperature in this pH range. A shift of the equilibrium toward $U(OH)_2^{2+}$, which is more reactive than U_{aq}^{4+} and UOH^{3+}, would provide the found changes in the glow intensity. In addition, the extent of exponential portions of the descending branches of the kinetic curves increases as temperature increases. For curve *1* (see Fig. 3) obtained at 285 K, the CL intensity decreases in the exponential portion by about an order of magnitude, whereas for curve *4* recorded at 310 K it decreases in the exponential portion by more than two orders of magnitude. All the kinetic dependences shown in Fig. 3 and in other figures are plotted in the form of semilogarithmic anamorphoses, *i.e.*, $\log I_{CL} = f(t)$. The linear portions of the curves (indicated by horizontal dashes in Fig. 3) were used for graphic determination of the reaction rate constants *k*. For a 0.001 *M* $HClO_4$ solution, the *k* values were found to be 31, 100, 162, and 667 L mol^{-1} s^{-1} (all with a 10% error) at 285, 293, 298, and 310 K, respectively. The temperature dependence of the rate constant of the reaction obeys the Arrhenius equation $E_a = 90.5\pm9$ kJ mol^{-1} (the correlation coefficient is 0.997). The *k* and E_a values for the $3 \cdot 10^{-4}$ *M* $HClO_4$ solution were determined with a somewhat higher degree of accuracy. At each of the three temperatures (282, 292.5, and 302 K), we carried out a series of four runs and obtained *k* values of 21.5±2.4, 73.3±3.0, and 204.6±11.5 L mol^{-1} s^{-1}, respectively, from which $E_a = 79.7\pm5.6$ kJ mol^{-1} (the correlation coefficient is 0.999). The activation energies found in this work are close to the known value $E_a = 89.9$ kJ mol^{-1}.[13]

Chemiluminescence allows monitoring of the course of the reactions characterized by changes in the concentrations of reagents by several orders of magnitude, which cannot be done using titrimetric or spectrophotometric technique. For instance, variations of the CL intensity (curve *4* in Fig. 3) and, hence, of the concentration of the substance responsible for the formation of $(UO_2^{2+})^*$ cover a range of four orders of magnitude.

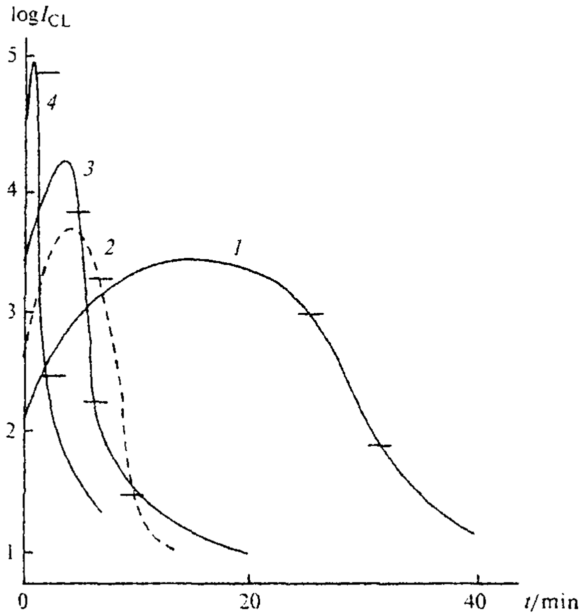

Fig. 3. Time profiles of the intensity of chemiluminescence (I_{CL}) accompanying the oxidation of U^{4+} by dioxygen at different temperatures ($[HClO_4]$ = 0.001 mol L^{-1}; $[U^{4+}]_0$ = $2.7 \cdot 10^{-5}$ mol L^{-1}): *T*/K = 285 (*1*), 293 (*2*), 298 (*3*), and 310 (*4*). Linear portions of the curves are indicated by horizontal dashes.

The kinetic curves do not always pass through a maximum. Extrema are found only at particular initial concentrations of U^{4+} in solutions. For instance, a monotonic decrease in the CL intensity occurs in 0.01 *M* $HClO_4$ solution at 313 K and $[U^{4+}]_0 = 5 \cdot 10^{-7}$ or $1 \cdot 10^{-6}$ mol L^{-1}. The increase in $[U^{4+}]_0$ up to $1 \cdot 10^{-5}$ mol L^{-1} gives rise to a maximum on the curve of the time profile of the CL intensity. Further increase in $[U^{4+}]_0$ causes an increase in I_{max} and shortening of t_{max}. The dependence of I_{max} on $[U^{4+}]$ can be linearized in log-log coordinates (Fig. 4, curve *1*). However, for analytical purposes it is more convenient to use the dependence of the CL light sum (*S*) on the initial concentration of U^{4+} in solution (see Fig. 4, curve *2*), since this makes it possible to decrease the lowest detectable concentration of U^{4+} down to 10^{-7} mol L^{-1}. It should be noted that chemiluminescent reactions of U^{4+} oxidation by Caro's acid ion (10^{-8} mol L^{-1})[12] and xenon trioxide (10^{-10} mol L^{-1})[7] have even greater analytical potentialities.

The oxidation of U^{4+} by dioxygen follows a chain-radical mechanism.[13] The water molecules and hydrogen ions in the left side of the equations are present in excess; therefore the constants *k* are bimolecular rather than trimolecular ones and their values are given here in L mol^{-1} s^{-1}:

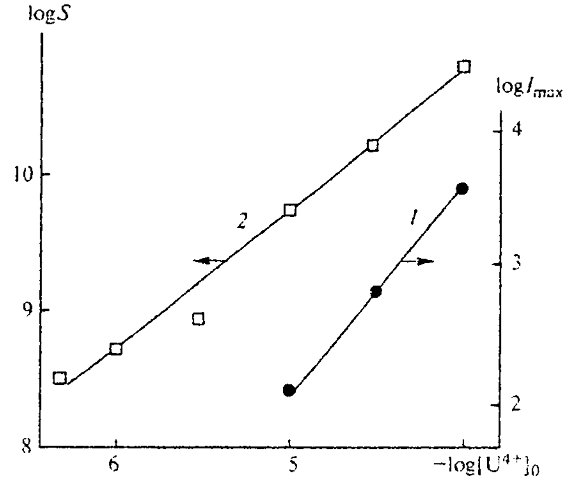

Fig. 4. The curves of the maximum CL intensity (I_{max}) (*1*) and the CL light sum (*S*) (*2*) as functions of U^{4+} concentration at 313 K ($[HClO_4]$ = 0.01 mol L^{-1}).

$$UOH^{3+} + O_2 + H_2O \longrightarrow UO_2^{+} + HO_2 + 2\,H^{+}, \quad k_3 \approx 10; \tag{3}$$

$$UO_2^{+} + O_2 + H^{+} \longrightarrow UO_2^{2+} + HO_2, \quad k_4 = 31; \tag{4}$$

$$UOH^{3+} + HO_2 + H_2O \longrightarrow UO_2^{+} + H_2O_2 + 2\,H^{+}; \tag{5}$$

$$UO_2^{+} + HO_2 + H_2O \longrightarrow UO_2^{2+} + H_2O_2 + OH^{-}, \quad 5 \cdot 10^5 < k_6 < 5 \cdot 10^7. \tag{6}$$

In this case, the UO_2^{+} ion and $HO_2^{\cdot}$ radical play the role of active centers. More recently, the reaction of U^{4+} oxidation by hydrogen peroxide has been studied,[14] which also proceeds by a chain-radical mechanism:

$$UOH^{3+} + H_2O_2 \longrightarrow UO_2^{+} + OH + 2\,H^{+}, \quad k_7 = 11; \tag{7}$$

$$UO_2^{+} + H_2O_2 + H^{+} \longrightarrow UO_2^{2+} + OH + H_2O, \quad k_8 = 1.7; \tag{8}$$

$$UOH^{3+} + OH \longrightarrow UO_2^{+} + 2\,H^{+}, \quad k_9 = 8 \cdot 10^8; \tag{9}$$

$$UO_2^{+} + OH + H^{+} \longrightarrow UO_2^{2+} + H_2O, \quad k_{10} \approx 10^9. \tag{10}$$

It seems likely that the reaction of U^{4+} with O_2 follows both pathways. The initiation reactions (3), (4), and (7) result in UO_2^{+} ions and in HO_2 and OH species, which are involved in the chain propagation stages (5), (8), and (9).*

Since $(UO_2^{2+})^*$ is the CL emitter, chemiluminescence can be observed in stages (4), (6), (8), and (10). However, the contributions of these reactions to the glow should differ appreciably because of different rate constants. We failed to detect CL in the reaction of O_2 with UO_2^{+} obtained by reduction of UO_2^{2+} with europium(II)[15]

$$UO_2^{2+} + Eu^{2+} \longrightarrow UO_2^{+} + Eu^{3+}. \tag{11}$$

Taking into account that the constant k_4 = 31 L mol^{-1} s^{-1} for a 0.005 *M* $HClO_4$ solution (see Ref. 16) is nearly 20 times higher than k_8 = 1.7 L mol^{-1} s^{-1} (see Ref. 17), one can conclude that the UO_2^{+} oxidation by hydrogen peroxide makes an insignificant contribution to experimentally recorded CL. We believe that reaction (10), consisting of electron transfer from UO_2^{+} to the $^{\cdot}OH$ radical, is the most plausible stage of the formation of the electron-excited uranyl ion. Based on the known[16] estimate, $5 \cdot 10^5$ L mol^{-1} s^{-1} < k_6 < $5 \cdot 10^7$ L mol^{-1} s^{-1}, the contribution of reaction (6) to the glow is at least two orders of magnitude smaller.

Let us consider possible reasons for the appearance of a maximum on the time profile of CL intensity in the oxidation of the U^{4+} ion by dioxygen. For the chemiluminescent stage (10) to proceed, it is necessary that the UO_2^{+} ion and $^{\cdot}OH$ radical be present in solution. These species are mainly formed in the reaction (7) between U^{4+} and H_2O_2. Hence, for the maximum CL intensity to be observed some time after the beginning of U^{4+} oxidation by dioxygen, accumulation of UO_2^{+} and H_2O_2 in solution is required. It is known that oxidation of UO_2^{+} by dioxygen produces hydrogen peroxide,[16] *i.e.*, this reaction proceeds in two stages, (4) and (6). It can be assumed that the reaction of U^{4+} with O_2 also leads to accumulation of H_2O_2 in solution. Indeed, we obtained the results, which can be explained by the formation and accumulation of H_2O_2 in a solution containing U^{4+} and O_2. If a portion of U^{4+} is repeatedly introduced into the solution after completion of U^{4+} oxidation by dioxygen, the initial CL intensity increases by a factor of 30 as compared to the I_0 value observed at the beginning of the reaction and a luminescence decay with an inflection in the region corresponding to the previously observed CL peak (Fig. 5, curves *1* and *2*, respectively) is recorded instead of the kinetic curve passing through a maximum. This was observed even if a U^{4+} solution was repeatedly introduced into the system several hours after completion of the reaction between U^{4+} and O_2.

Taking into account the stepwise hydrolysis of U^{4+}, the expression for the rate constant of the reaction of U^{4+} with O_2 has the following form[2]:

$$k_3 = (k'[H^{+}] + k'')/([H^{+}]^2 + K_1[H^{+}] + K_2),$$

where, according to our data, k' = $1.5 \cdot 10^{-2}$ s^{-1}, k'' = $2.4 \cdot 10^{-3}$ L mol^{-1} s^{-1}. Assuming that this expression is also valid for the pH range between 2 and 3, we get $k_3 \approx 10$ L mol^{-1} s^{-1} (for a 0.005 *M* $HClO_4$ solution).

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* For clarity, the reactions which proceed involving U_{aq}^{4+} and $U(OH)_2^{2+}$ ions are not shown. In addition, the formulas of both radical and radical cation species ($HO_2^{\cdot}$, $UO_2^{\cdot +}$, *etc.*) are given without indicating the unpaired electron.

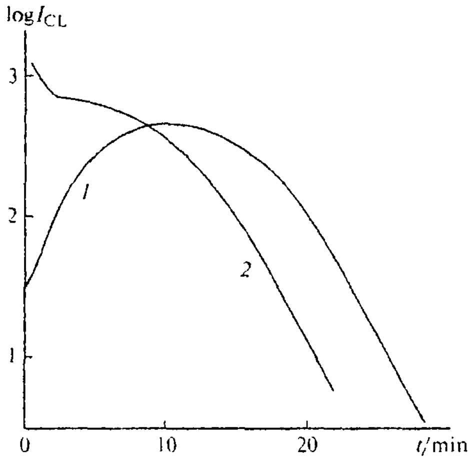

Fig. 5. Time profiles of the intensity of chemiluminescence (I_{CL}) accompanying the reaction of U^{4+} with O_2 (*1*) and the curve of chemiluminescence decay after repeated introduction of U^{4+} into the solution after completion of the reaction of oxidation of U^{4+} by dioxygen (*2*) at 313 K ([$HClO_4$] = 0.01 mol L^{-1}; $[U^{4+}]_0 = 1 \cdot 10^{-5}$ mol L^{-1}).

Therefore, the constant k_3 is only 3 times lower than k_4. It is known that the rate of U^{4+} oxidation by hydrogen peroxide is much higher than that of the reaction of U^{4+} with O_2.[2] At the same time, the rate constant of UO_2^+ oxidation by hydrogen peroxide (k_8 = 1.7 L mol^{-1} s^{-1} for a 0.005 *M* $HClO_4$ solution)[17] appears to be lower than k_7. The rate constant k_7 of the reaction of U^{4+} with O_2 in a 0.17 *M* $HClO_4$ solution is 11 L mol^{-1} s^{-1}.[2] Taking into account that k_7 is inversely proportional to [H^+], the k_7 value for a 0.005 *M* $HClO_4$ solution should be much higher. It seems likely that not only H_2O_2, but also UO_2^+, can accumulate in the course of the reaction between U^{4+} and O_2. If so, the appearance of a maximum on the kinetic curve is due to the accumulation of UO_2^+ ions in the solution. Fast oxidation of these ions by $^{\cdot}OH$ radicals is accompanied by the formation of uranyl ions, a fraction of which can be in the excited state. The intensity of experimentally recorded CL is proportional to the concentration of uranyl ions in the electron-excited state.

We found that the chemiluminescent stage of U^{4+} oxidation by dioxygen in 0.01 *M* $HClO_4$ solution is rather sensitive to the presence of UO_2^{2+} ions. The time profiles of the intensity of CL accompanying the oxidation of U^{4+} in solutions containing no UO_2^{2+} and in the presence of uranyl ions are shown in Fig. 6. At [UO_2^{2+}] = $81.2 \cdot 10^{-5}$ mol L^{-1}, the I_{max} value increases by nearly two orders of magnitude; t_{max} is shortened by an order of magnitude (from 18 to 1.5 min); and the rate constant increases by a factor of 50 (from 1.7 to 85 L mol^{-1} s^{-1}). Hence, it is believed that a catalytic effect of UO_2^{2+} ions takes place. The descending portion of the kinetic curve for the concentration of UO_2^{2+} can be satisfactorily linearized in log-log coordinates (Fig. 7, curve *1*). The CL yield also increases in the presence of UO_2^{2+} (see Fig. 7, curve *2*).

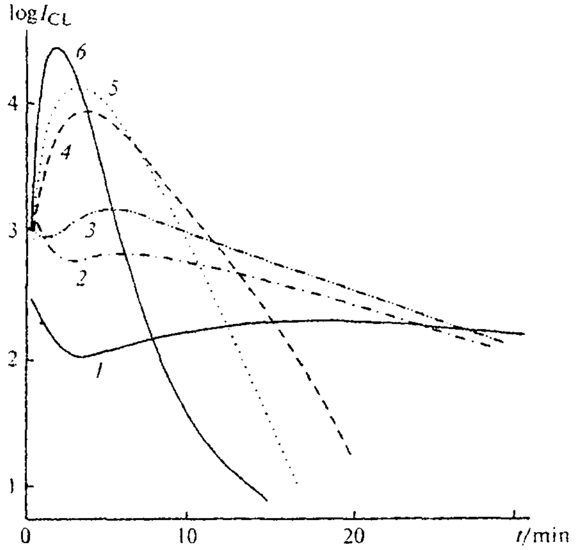

Fig. 6. Kinetic curves of chemiluminescence accompanying the reaction of U^{4+} with O_2 in the presence of uranyl ions at 313 K ([$HClO_4$] = 0.011 mol L^{-1}; $[U^{4+}]_0 = 1.5 \cdot 10^{-5}$ mol L^{-1}): [UO_2^{2+}]/mol L^{-1} = 0 (*1*), $1.2 \cdot 10^{-5}$ (*2*), $3.2 \cdot 10^{-5}$ (*3*), $11.2 \cdot 10^{-5}$ (*4*), $21.2 \cdot 10^{-5}$ (*5*), and $81.2 \cdot 10^{-5}$ (*6*).

The formation of the $UO_2^+ \cdot UO_2^{2+}$ cation-cation complex[15,18] may be the most plausible reason for the acceleration of the reaction. Previously,[15] it has been shown that the disproportionation rate of uranium(v) in the complex with UO_2^{2+} is much lower than that of free UO_2^+:

$$2\ UO_2^+ + 4\ H^+ \xrightarrow{K_{12}} UO_2^{2+} + U^{4+} + 2\ H_2O. \qquad (12)$$

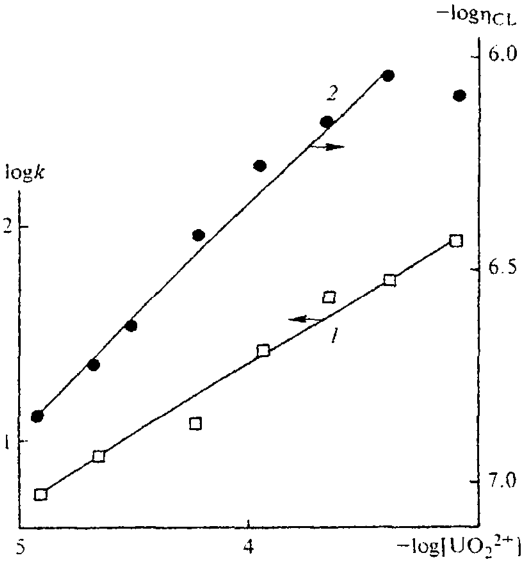

Fig. 7. The curves for the rate constant of the reaction (*k*) (*1*) and the CL yield (η_{CL}) (*2*) as functions of the concentration of uranyl ion in a solution containing U^{4+} and O_2 at 313 K ([$HClO_4$] = 0.011 mol L^{-1}; $[U^{4+}]_0 = 1.5 \cdot 10^{-5}$ mol L^{-1}).

We believe that the scheme of the mechanism of U^{4+} oxidation by dioxygen (see above) should be augmented with reaction (12). In the presence of UO_2^{2+} the contribution of reaction (12) to the quenching of active center (UO_2^+) decreases and chain oxidation of U^{4+} proceeds more efficiently.

The reverse (with respect to disproportionation of UO_2^+) reaction also can affect the concentration of UO_2^+ in solution. According to published data,[19] the equilibrium constant of reaction (12)

$$K_{12} = [U^{4+}] \cdot [UO_2^{2+}]/([UO_2^+]^2 \cdot [H^+]^4)$$

is $1.02 \cdot 10^9$ for $\mu = 2$ and $T = 298$ K (*cf.* Ref. 20: $K_{12} = 1.7 \cdot 10^6$). The rate constant for disproportionation decreases as pH increases and μ decreases, so that the K_{12} value cannot be too high under these conditions. This is confirmed by the data on the formation of a considerable amount of UO_2^+ by mixing the U^{4+} and UO_2^{2+} solutions in a HCl solution at pH 2.5.[21] Setting $K_{12} \approx 10^6$, under conditions of our experiments (pH 2, $[U^{4+}]_0 = 10^{-5}$ mol L^{-1}, $[UO_2^{2+}] = 10^{-5}$—10^{-3} mol L^{-1}) we find that the concentration of UO_2^+ can reach 10^{-8}—10^{-6} mol L^{-1} (0.1—10% of the initial concentration of U^{4+}). Therefore, the uranyl ion plays a double role. On the one hand, it retards the chain termination reaction (disproportionation of UO_2^+). On the other hand, it is involved in the regeneration of the active center UO_2^+, which favors faster chain-radical oxidation of U^{4+} by dioxygen.

Establishment of the reasons for the eight-fold increase in the CL yield in the presence of only $4 \cdot 10^{-4}$ mol L^{-1} UO_2^{2+} at fixed pH and temperature requires additional experiments and analysis of published data on the photophysical and photochemical processes proceeding with the participation of $(UO_2^{2+})^*$. As of now, we can only assume that the change in the CL yield is due to the presence of the $UO_2^+ \cdot UO_2^{2+}$ complex. Probably, the oxidation of $UO_2^+ \cdot UO_2^{2+}$ by $^{\cdot}OH$ radical results in the formation of a hypothetical complex with one $(^*UO_2^{2+} \cdot UO_2^{2+})$ or both $(UO_2^{2+} \cdot UO_2^{2+})^*$ uranyl ions in the excited state.

There are two ways of radiationless deactivation of $(UO_2^{2+})^*$, which are conventionally called physical deactivation and chemical quenching.[22] In the first case, conversion of the electronic excitation energy to thermal energy occurs owing to the activation of vibrational modes of the O—H bonds of water molecules in the coordination sphere of the uranyl ion. In the case of "chemical quenching" the $(UO_2^{2+})^*$ ion, which is a strong oxidizing agent (E = 2.6—2.7 V), reacts with the water molecule

$$(UO_2^{2+})^* + H_2O \longrightarrow UO_2^+ + OH + H^+. \qquad (13)$$

In the complex, the $(UO_2^{2+})^*$ ion has a smaller number of water molecules in the coordination sphere; hence the probability of radiationless relaxation of the electronic excitation energy decreases. The excited uranyl ion, which forms a complex with, *e.g.*, ClO_4^-, is characterized by reduced oxidative ability toward H_2O.[23] It seems likely that the $^*UO_2^{2+} \cdot UO_2^{2+}$ complex behaves analogously.

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