

# Autoacceleration of the Free-Radical Chain Luminescent Oxidation of U(IV) with Xenon Trioxide in Aqueous HClO<sub>4</sub>

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Received March 14, 2006; in final form, April 27, 2007

**Abstract**—Autoacceleration is observed in the chemiluminescent radical chain oxidation of U(IV) with xenon trioxide in aqueous perchloric acid in a Teflon (not conventional glass) reactor. The decay of chemiluminescence accompanying the reaction between U(IV) and XeO<sub>3</sub> in the case of excess oxidizer obeys a first-order kinetic equation only at low U(IV) concentrations of 10<sup>-5</sup>–10<sup>-6</sup> mol/l. Autoacceleration takes place at comparatively high reactant concentrations, when the contribution from the heterogeneous loss of radicals on the reactor walls into chain termination is comparatively small and the role of degenerate chain branching reactions is significant. It is inferred that a critical phenomenon rare for liquid-phase radical chain processes takes place in U(IV) oxidation with xenon trioxide: a comparative small increase in the reactant concentrations causes this chemiluminescent redox process to pass from the quasi-steady-state regime to autoacceleration.

DOI: 10.1134/S0023158408010047

Among the known inorganic chemiluminescent redox processes, the reactions of low-valence uranium species in aqueous solutions of sulfuric and perchloric acids have attracted the greatest interest. Investigation of these reactions has provided quantitative estimates for the effects of the nature of the oxidizer and solvent, the acidity of the medium, complex formation processes, temperature, and the phase and isotope composition of the solution on the efficiency of chemical-to-light energy conversion. Among the above processes, the oxidation of U(IV) with xenon trioxide [1, 2] is characterized by the highest yield of chemiluminescence (CL), which is emitted by the electronically excited uranyl ion  $^*(\text{UO}_2^{2+})$ . The high luminance from the reaction between U(IV) and XeO<sub>3</sub> makes it possible to monitor this reaction at reactant concentrations that are hundreds or even thousands of times lower than the concentrations sufficient for spectrophotometry.

The heterogeneous decay of radicals at the solid/liquid interface can slow down the radical chain reaction under certain conditions. It is of interest to study the chemiluminescent oxidation of U(IV) with xenon trioxide in an HClO<sub>4</sub> solution placed not in a glass vessel, but in a Teflon reactor, in which the probability of the heterogeneous decay of radicals is ten times lower [3].

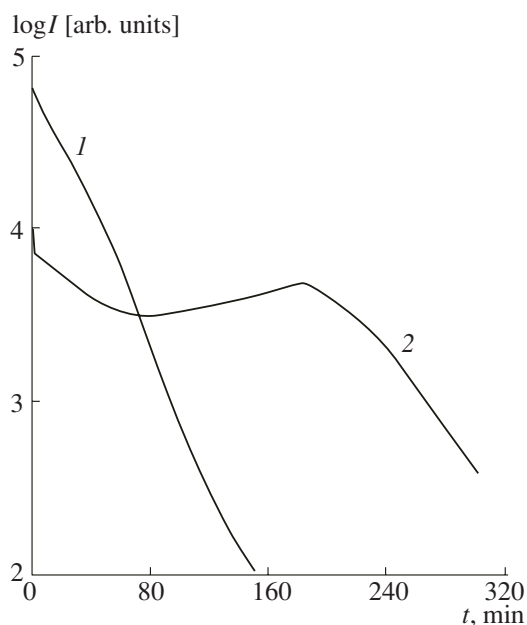
Here, we report that the kinetics of the reaction depends strongly on the initiation conditions, namely, the initial U(IV) concentration, the way and order in which the oxidizer and the reductant are introduced into the solutions of the reductant and oxidizer, respectively, and the duration of stirring of one reductant in solution before the addition of the other. We observed well-pronounced autoacceleration in the luminescent reaction

between U(IV) and XeO<sub>3</sub> in aqueous HClO<sub>4</sub> at comparatively high reactant concentrations.

## EXPERIMENTAL

The CL detection equipment, synthesis and purification procedures, and solution preparation are described elsewhere [4, 5]. The reaction was carried out in a cylindrical Teflon reactor 38 mm in diameter under stirring. The temperature was maintained within  $\pm 0.1$  K. Twice-distilled water to be used in solution preparation was heated to 373 K before use in order to reduce the concentration of dissolved atmospheric oxygen. A fresh, argon-bubbled solution of U(IV) (10<sup>-2</sup> mol/l) in 1 M HClO<sub>4</sub> was stored no longer than 1 day in a tightly stoppered Pyrex flask at 273 K. Next, a small amount (5–100  $\mu\text{l}$ ) of this concentrated U(IV) solution was micropipetted to 10 ml of a 0.1–1.0 M HClO<sub>4</sub> solution in the reactor. In some cases, less concentrated uranium solutions in 1 M HClO<sub>4</sub> were prepared at 273 K. The reaction temperature was continuously measured with a copper–constantan thermocouple sealed in a thin-walled glass capillary. The stirrer assembly was made of Teflon and consisted of a shaft with a two-blade propeller secured to it. The stirrer was actuated with a miniature electromotor.

The photometric unit, with an FEU-140 photomultiplier, was calibrated against a standard radioluminescence source, which was a liquid scintillator (toluene solution of diphenyloxazole and diphenyloxazolybenzene) containing <sup>14</sup>C-labeled acetic acid. The CL yield ( $\eta_{\text{CL}}$ ) was determined as the ratio of the chemiluminescence light sum ( $S$ ) to the initial U(IV) concentration in



**Fig. 1.** Time dependence of the CL intensity for the oxidation of U(IV) with xenon trioxide ( $[\text{XeO}_3]_0 = 1 \times 10^{-4}$  mol/l) in 1 M solutions: (1)  $\text{H}_2\text{SO}_4$  ( $[\text{U(IV)}]_0 = 2.5 \times 10^{-5}$  mol/l,  $T = 293$  K) and (2)  $\text{HClO}_4$  ( $[\text{U(IV)}]_0 = 1 \times 10^{-5}$  mol/l,  $T = 298$  K).

the solution:  $\eta_{\text{CL}} = S/[\text{U(IV)}]_0$ . The light sum (in einsteins per liter) was found using the formula

$$S = \frac{P}{P_{\text{st}}} I_{\text{st}} \frac{1000}{V} \frac{1}{N_A},$$

where  $P = \int I_{\text{CL}} dt$  is the area under the curve of CL intensity versus time ( $I_{\text{CL}} = f(t)$ ),  $P_{\text{st}} = \int I_{\text{st}} dt$  is the same for the standard light source,  $I_{\text{st}}$  is the intensity of light from the standard source ( $(9.8 \pm 0.4) \times 10^7$  photon/s),  $V$  is the volume of the solution (ml), and  $N_A$  is Avogadro's number.

In the general case, the CL yield may vary during the reaction. The  $\eta_{\text{CL}}$  determination technique used in this study allowed us to find only the CL yield averaged over a particular run after the completion of the run. However, if different  $\eta_{\text{CL}}$  values are measured in different runs for the same system at the same temperature, then the emitter excitation yields ( $\eta_{\text{exc}}$ ) are also different because  $\eta_{\text{CL}} = \eta_{\text{exc}} \eta_{\text{em}}$  and the emission yield  $\eta_{\text{em}}$  is always constant. Therefore, excitation yield variation would be evidence of changes taking place in the reaction mechanism.

## RESULTS AND DISCUSSION

The chemiluminescent oxidation of U(IV) with xenon trioxide in aqueous 0.2–1.0 M  $\text{H}_2\text{SO}_4$  solutions

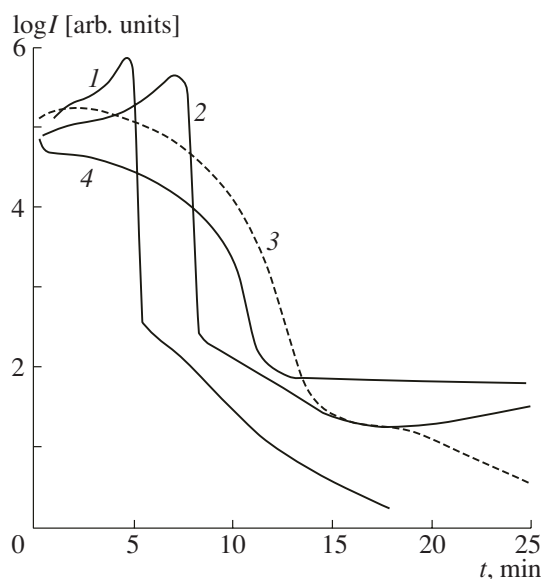
containing excess oxidizer is first-order [2, 6, 7]. We expected that the kinetics of the reaction between U(IV) and  $\text{XeO}_3$  in aqueous 1 M  $\text{HClO}_4$  in a Teflon reactor would not be more complicated. We chose 1 M  $\text{HClO}_4$  as the solvent for the reason that U(IV) does not form any complex with the  $\text{ClO}_4^-$  anion in this medium

and exists mainly as the aqua cation  $\text{U}_{\text{aq}}^{4+}$  [8] and the concentration of the hydroxo species  $\text{UOH}^{3+}$  is insignificant [9]. In fact, it turned out that the kinetics of the reaction in 1 M  $\text{HClO}_4$  is quite different from the kinetics of the reaction in 1 M  $\text{H}_2\text{SO}_4$  (Fig. 1, curves 1, 2). In 1 M  $\text{HClO}_4$ , as distinct from 1 M  $\text{H}_2\text{SO}_4$  (curve 1), there is no monotonic decay of luminescence and the process is described by a complicated kinetic curve resembling the time profile of CL intensity for 1 M  $\text{H}_2\text{SO}_4$  containing U(IV),  $\text{XeO}_3$ , and  $\text{H}_2\text{O}_2$  [10]. Initially, the CL intensity decreases exponentially and the duration of this initial decay can be viewed as the induction period. After that, the CL intensity increases, passes through a maximum, and then falls again.

The rate of U(IV) oxidation with xenon trioxide in 1 M  $\text{HClO}_4$  is not high: at  $T = 298$  K,  $[\text{U(IV)}]_0 = 10^{-5}$  mol/l, and  $[\text{XeO}_3]_0 = 10^{-4}$  mol/l, the reaction lasts longer than 5 h (Fig. 1, curve 2). In order to quicken the experiment, we raised the reaction temperature from 298 to 306 K and reduced the acid concentration by one order of magnitude. This shortened the reaction time by a factor of 10–20 and raised the maximum luminance at the same initial reactant concentrations by 2–3 orders of magnitude.

Here, it is necessary to make the following remark. The reaction time was taken to be equal to the interval between the instant CL appeared after the mixing of the reactants and the instant the CL disappeared or, more precisely, fell down to the photomultiplier noise level. Special-purpose experiments demonstrated that the initial intensity of the CL accompanying the reaction between U(IV) and  $\text{XeO}_3$  is proportional to the U(IV) concentration. It is conventionally assumed that the CL intensity is proportional to the rate of dark oxidation and this proportionality is invariable throughout the reaction. However, we will demonstrate below that, under some conditions, the CL yield varies during the reaction between U(IV) and  $\text{XeO}_3$  and this variation is likely due to the change of the reaction mechanism.

The chemiluminescent reaction in question shows autoacceleration. For example, after the reductant (5  $\mu\text{l}$  of a  $10^{-2}$  mol/l U(IV) solution in 1 M  $\text{HClO}_4$ ) is introduced into the reactor containing 9 ml of  $\text{H}_2\text{O}$  and 0.8 ml of 1 M  $\text{HClO}_4$  and then, after some period of time ( $\Delta t$ ), the oxidizer (0.2 ml of a  $5 \times 10^{-3}$  mol/l  $\text{XeO}_3$  solution in 1 M  $\text{HClO}_4$ ) is added, the CL intensity initially rises to its maximum value ( $I_{\text{max}}$ ) and then falls off sharply by a factor of several thousands. After that, the kinetic trace indicates a slower CL decay (Fig. 2, curve 1). Note that, in all the plots presented in this article, the ordinate axis is logarithmic. As  $\Delta t$  increases, the

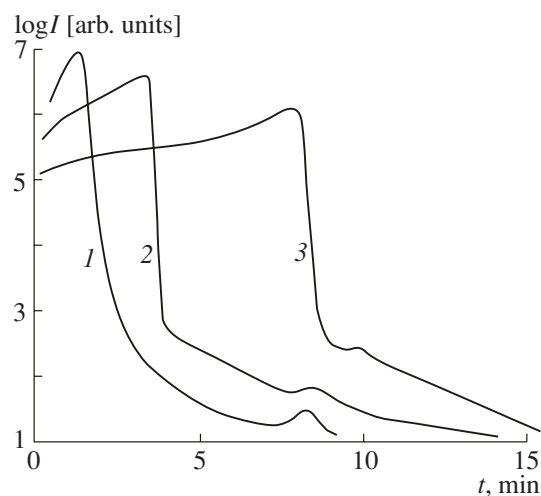


**Fig. 2.** Kinetics of CL accompanying the reaction between U(IV) and  $\text{XeO}_3$  for different time intervals ( $\Delta t$ ) between the introduction of  $5 \mu\text{l}$  of a  $10^{-2} \text{ mol/l}$  U(IV) solution in  $1 \text{ M HClO}_4$  into the reactor containing  $9 \text{ ml}$  of  $\text{H}_2\text{O}$  and  $0.8 \text{ ml}$  of  $1 \text{ M HClO}_4$  and the addition of  $0.2 \text{ ml}$  of a  $5 \times 10^{-3} \text{ mol/l}$   $\text{XeO}_3$  solution in  $1 \text{ M HClO}_4$ .  $\Delta t = (1) 8, (2) 15, (3) 30$ , and  $(4) 180 \text{ s}$ .  $[\text{XeO}_3]_0 = 10^{-4} \text{ mol/l}$ ,  $[\text{U(IV)}]_0 = 5 \times 10^{-6} \text{ mol/l}$ ,  $T = 306 \text{ K}$ , continuous stirring.

rate of increase of the CL intensity decreases, the  $I_{\max}$  time increases, the  $I_{\max}$  value itself decreases, and the postmaximum decline of the CL intensity becomes more gentle (Fig. 2).

Consider the inverse order of mixing the reactants. After the oxidizer ( $0.2 \text{ ml}$  of a  $5 \times 10^{-3} \text{ mol/l}$   $\text{XeO}_3$  solution in  $1 \text{ M HClO}_4$ ) is poured into the reactor containing  $9 \text{ ml}$  of  $\text{H}_2\text{O}$  and  $0.8 \text{ ml}$  of  $1 \text{ M HClO}_4$  and then, after a period of time  $\Delta t$ , the reductant ( $10 \mu\text{l}$  of a  $10^{-2} \text{ mol/l}$  U(IV) solution in  $1 \text{ M HClO}_4$ ) is added, both an increase in the CL intensity and a luminance peak in the kinetic curve are observed again (Fig. 3). By comparing curves 1 in Figs. 2 and 3, one can see that changing the reactant mixing order and increasing the amount of U(IV) by a factor as small as 2 raise  $I_{\max}$  by one order of magnitude and reduce the  $I_{\max}$  time by a factor of 3 (from  $4.5$  to  $1.5 \text{ min}$ ). This brings up the following questions: What is the mechanism of the acceleration of the reaction between U(IV) and  $\text{XeO}_3$ ? And why does the kinetics of this reaction depend so strongly on  $\Delta t$ ?

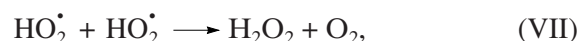
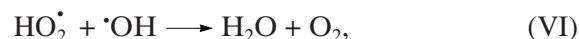
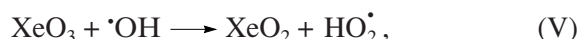
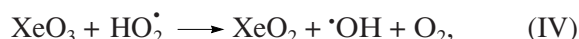
For the experiment in which U(IV) was kept for a period of time  $\Delta t$  in a  $0.08 \text{ M HClO}_4$  solution that was in contact with the atmosphere and, as a consequence, contained approximately  $10^{-4} \text{ mol/l}$  of oxygen, the initial decline of the CL intensity might seem to be due to the trivial decrease in  $[\text{U(IV)}]_0$  as a result of the reaction between U(IV) and  $\text{O}_2$ . However, as was demonstrated in our earlier work [11], the rate of U(IV) oxidation with atmospheric oxygen in  $0.08 \text{ M HClO}_4$  at  $306 \text{ K}$  is



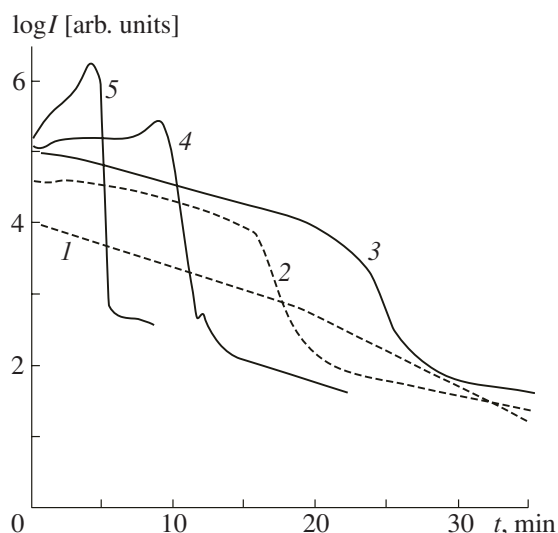
**Fig. 3.** Kinetics of CL accompanying the reaction between U(IV) and  $\text{XeO}_3$  for different time intervals ( $\Delta t$ ) between the introduction of  $0.2 \text{ ml}$  of a  $5 \times 10^{-3} \text{ mol/l}$   $\text{XeO}_3$  solution in  $1 \text{ M HClO}_4$  into the reactor containing  $9 \text{ ml}$  of  $\text{H}_2\text{O}$  and  $0.8 \text{ ml}$  of  $1 \text{ M HClO}_4$  and the addition of  $10 \mu\text{l}$  of a  $10^{-2} \text{ mol/l}$  U(IV) solution in  $1 \text{ M HClO}_4$ .  $\Delta t = (1) 15, (2) 60$ , and  $(3) 180 \text{ s}$ .  $[\text{XeO}_3]_0 = 10^{-4} \text{ mol/l}$ ,  $[\text{U(IV)}]_0 = 10^{-5} \text{ mol/l}$ ,  $T = 306 \text{ K}$ , continuous stirring.

low (the rate constant is  $k = 6\text{--}8 \text{ l mol}^{-1} \text{ s}^{-1}$ ). Only little of the U(IV) will be oxidized in  $180 \text{ s}$ . This is also indicated by the approximately equal CL intensities at the initial stages of the reaction (Fig. 2).

If so, then is not it possible that the oxidizer concentration decreases markedly in the time period  $\Delta t$ ? Aqueous solutions of xenon trioxide are known to be unstable because of  $\text{XeO}_3$  undergoing free-radical chain decomposition [12]:



The  $\text{XeO}_3$  decomposition rate constant at  $\text{pH } 1$  and  $T = 363 \text{ K}$  is  $k = 10^{-4} \text{ s}^{-1}$ , and the activation energy of thermolysis at  $T = 355\text{--}371 \text{ K}$  is  $E_a = 106.8 \text{ kJ/mol}$  [12]. Under the assumption that  $E_a$  is the same at lower temperatures, the rate constant of xenon trioxide thermoly-

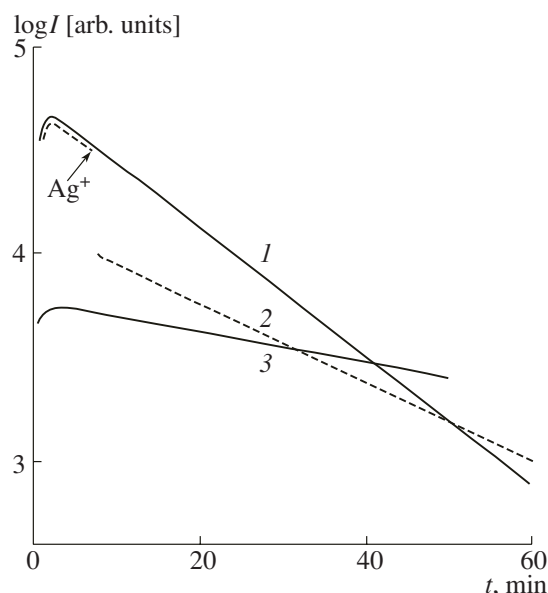


**Fig. 4.** Kinetics of CL after the introduction of (1–4)  $10^{-3}$  and (5)  $10^{-2}$  mol/l U(IV) solutions in 1 M  $\text{HClO}_4$  into the reactor containing a  $\text{XeO}_3$  solution in 0.1 M  $\text{HClO}_4$ . The volume of the U(IV) solution added is (1) 25, (2) 50, (3) 90, (4) 100, and (5) 10  $\mu\text{l}$ .  $[\text{XeO}_3]_0 = 10^{-4}$  mol/l,  $T = 306$  K, and  $\Delta t = 15$  s.

sis under our experimental conditions ( $T = 306$  K) is  $k = 5 \times 10^{-7} \text{ s}^{-1}$ . Since  $[\text{XeO}_3]_0 = 10^{-4}$  mol/l, the oxidizer concentration after 180 s will be  $\sim 10^{-8}$  mol/l (0.01%) lower. Obviously, when the oxidizer is in tenfold excess in the solution, this small decrease in its concentration cannot exert any significant effect on the kinetics of the reaction.

Experiments demonstrated that the kinetics of U(IV) oxidation with xenon trioxide in 0.1 M  $\text{HClO}_4$  depends on  $[\text{U(IV)}]_0$  (Fig. 4). Figure 4 plots the time profiles of the CL intensity for the series of experiments in which 0.2 ml of a  $5 \times 10^{-3}$  mol/l  $\text{XeO}_3$  solution in 1 M  $\text{HClO}_4$  is introduced into the reactor containing 9 ml of  $\text{H}_2\text{O}$  and 0.8 ml of 1 M  $\text{HClO}_4$  and, after 15 s, different volumes of a  $1 \times 10^{-3}$  mol/l U(IV) solution in 1 M  $\text{HClO}_4$  are added. The concentration of the oxidizer at the instant it comes into contact with U(IV) is nearly the same in this series of experiments because the solution stirring conditions, as well as the conditions of  $\text{XeO}_3$  loss due to thermal decomposition, are nearly invariable. In the case of 25  $\mu\text{l}$  of the U(IV) solution added to the  $\text{XeO}_3$  solution ( $[\text{U(IV)}]_0 = 2.5 \times 10^{-6}$  mol/l (provided that the uranium solution is uniformly distributed in the reaction mixture), the reaction is described by a first-order rate equation, as is indicated by the strictly exponential decline of the CL intensity over the first 20 min (Fig. 4, curve 1).

Raising the volume of the U(IV) solution to 50  $\mu\text{l}$  and then 90  $\mu\text{l}$  causes an increase in the initial luminance and gives rise to inflections in the kinetic trace 15–20 min after the beginning of the interaction



**Fig. 5.** Time dependences of the CL intensity for U(IV) oxidation with xenon trioxide (1) in the absence of  $\text{Ag}^+$ , (2) before and after adding  $10^{-6}$  mol/l  $\text{Ag}^+$  to the solution, and (3) in the presence of  $10^{-5}$  mol/l  $\text{Ag}^+$ .  $[\text{U(IV)}]_0 = 10^{-5}$  mol/l,  $[\text{XeO}_3]_0 = 5 \times 10^{-5}$  mol/l, 0.1 M  $\text{HClO}_4$ , and  $T = 298$  K.

between U(IV) and  $\text{XeO}_3$ . At the same time, the  $\log I$  versus  $t$  curves retain extensive exponential portions (Fig. 4, curves 2, 3). The kinetics of the reaction is different in the case of 100  $\mu\text{l}$  of the U(IV) solution added to the  $\text{XeO}_3$  solution, when  $[\text{U(IV)}]_0 = 10^{-5}$  mol/l (Fig. 4, curve 4).

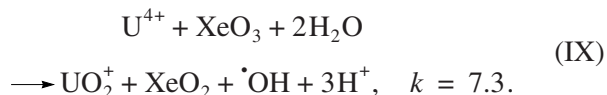
Thus, it follows from Fig. 4 that the autoaccelerated kinetic regime takes place only after some critical U(IV) concentration is exceeded. The highest luminescence ignition rate and the highest luminance are reached when not 100  $\mu\text{l}$  of the  $10^{-3}$  mol/l U(IV) solution in 1 M  $\text{HClO}_4$  is introduced into the oxidizer solution, but when a ten times smaller volume (10  $\mu\text{l}$ ) of the 10 times more concentrated ( $10^{-2}$  mol/l) U(IV) solution in 1 M  $\text{HClO}_4$  is added (Fig. 4, curve 5). In this case, the local U(IV) concentration immediately after the introduction of U(IV) is higher than the same concentration in the run described by curve 4 in Fig. 4.

This finding and the data presented in Figs. 2 and 3 suggest that autoacceleration in the luminescent oxidation of U(IV) with xenon trioxide takes place when the local concentrations of the reactants far exceed their concentrations resulting from the uniform distribution of the oxidizer and reductant molecules throughout the solution volume. For example, after a concentrated solution of U(IV) is added to a  $\text{XeO}_3$  solution, the local concentration of the former decreases during stirring. When it approaches the stoichiometric value, the reaction can proceed at a much higher rate than in the case of the uniform distribution of the reactants throughout the reactor volume.

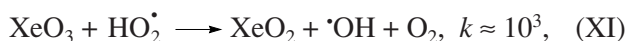


Below, we suggest a radical chain mechanism for U(IV) oxidation with xenon trioxide. In this mechanism, the elementary step yielding the CL emitter, which is the electronically excited uranyl ion  $^*(\text{UO}_2^{2+})$ , is electron transfer from the  $\text{UO}_2^+$  ion to the oxidizer, which is the  $\cdot\text{OH}$  radical. This mechanism includes the following steps (the water molecules and hydrogen ions appearing on the left-hand sides of the equations are in excess; therefore, the constants  $k$  are bimolecular, not trimolecular, and have dimensions of  $\text{l mol}^{-1} \text{s}^{-1}$ ):

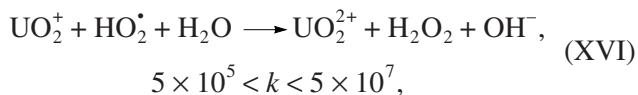
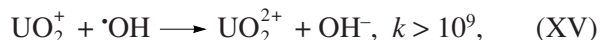
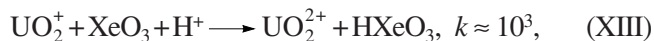
Chain initiation:



Chain propagation:



Chain termination:



Chain termination is also caused by radical recombination reactions (VI)–(VIII).

The choice of reaction (XV) as the emitter formation step is based on the following fundamental principle of CL theory: the formation of excited states takes place in those reactions in which the “structural similarity” principle is obeyed. In other words, efficient excitation is possible only when the activated complex is structurally similar to the excited reaction product. This principle is readily obeyed by chemiluminescent electron transfer reactions, in which no chemical bonds break or form and, accordingly, any nuclear rearrangement in the molecules is ruled out. In the single-step oxidation of U(IV) to  $\text{UO}_2^{2+}$ , the coordination bond U–O shortens from 2.3 to 1.8 Å. This yields a very “hot” (vibrationally excited) uranyl ion with an equivalent temperature of several hundreds of degrees Celsius. This must cause the thermal deactivation of the electronically excited states of the uranyl ion and

quench CL. If the structural similarity principle is indeed a rule, then the elementary step responsible for  $\text{UO}_2^{2+}$  excitation is different and must be electron transfer from the uranyl ion to the oxidizer.

We believe that the interaction between U(IV) and  $\text{XeO}_3$  is a degenerate branched-chain reaction. For branched-chain reactions, the concentration of free radicals ( $n$ ) as a function of the ratio of the rate constants of chain branching ( $f$ ) and termination ( $g$ ) can be governed by two different laws. In the case of linear-law chain termination, the rate equation for the active sites of the chain reaction is

$$\frac{dn}{dt} = v_0 + fn - gn, \quad \text{or} \quad \frac{dn}{dt} = v_0 + \phi n, \quad (1)$$

where  $v_0$  is the chain initiation rate and  $\phi = f - g$ . Two variants are possible here.

(1) If  $f < g$  ( $\phi = f - g < 0$ ), integration of Eq. (1) yields the following expression describing the buildup of radicals in the system [13]:

$$n = (v_0/\phi)[1 - e^{-\phi t}]. \quad (2)$$

According to Eq. (2), a quasi-steady-state radical concentration will be established in the system after a time:

$$n = v_0/\phi = v_0/(g - f). \quad (3)$$

In this case, chain branching only increases the quasi-steady-state value of  $n$  relative to the  $n$  value at  $f = 0$ . This is equivalent to some decrease in the chain termination rate. Therefore, a quasi-steady state chain reaction takes place in the system and its kinetic characteristics do not differ radically from the characteristics of nonbranched chain reactions. We believe that it is this U(IV)– $\text{XeO}_3$  interaction regime that takes place at low reactant concentrations, when, if the oxidizer is in excess, the chemiluminescent reaction obeys a first-order rate equation. In this case, the loss of radicals on the reactor wall surface is comparable with the total radical content of the reaction mixture and the effective rate constant of chain termination is  $g > f$ .

(2) If  $f > g$  (i.e.,  $\phi > 0$ ), integration of Eq. (1) yields the following expression [13]:

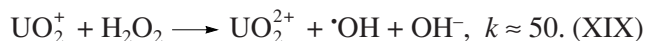
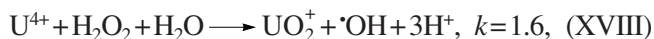
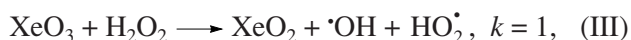
$$n = (v_0/\phi)[e^{\phi t} - 1] \quad \text{or, for } \phi t > 1, \quad n \approx (v_0/\phi)e^{\phi t}. \quad (4)$$

In this case, the concentration of free radicals and, accordingly, the rate of the chain reaction increase progressively. It is this autoaccelerated kinetic regime that takes place when a small volume of a comparatively concentrated solution of the oxidizer or reductant is introduced into the reactor. The local concentration of the reactants in this case can be tens or even hundreds of times higher than their concentration in the case of the uniform distribution of reacting molecules throughout the reactor volume.

Thus, the longer  $\Delta t$ , the longer the stirring time for the reactant that was introduced first and, therefore, the lower the local concentration of this reactant in the solution. The effect of the reactant mixing order on the kinetics of the reaction is primarily due to the fact that

the local U(IV) concentration in the stirred reactor at the instant  $\text{XeO}_3$  is added is lower (Fig. 2) than the same concentration in the case of  $10\ \mu\text{l}$  of a  $10^{-2}\ \text{mol/l}$  U(IV) solution added to the stirred  $\text{XeO}_3$  solution (Fig. 3). At  $\Delta t = 15\ \text{s}$ ,  $I_{\text{max}}$  is 10 times larger in the latter case than in the former case (compare curves 1 in Figs. 3 and 2, respectively).  $\eta_{\text{CL}}$  is also larger in the latter case ( $9 \times 10^{-5}$  versus  $4.4 \times 10^{-5}$ ). The higher CL yield can be attributed to the fact that a larger fraction of the  $\cdot\text{OH}$  radicals formed in the solution participates in the light-emitting step of the reaction.

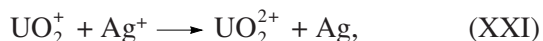
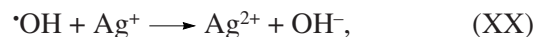
We believe that the autoacceleration of the redox process is due to  $\text{H}_2\text{O}_2$  participating in it. The reactions involving hydrogen peroxide are believed to cause degenerate chain branching. Hydrogen peroxide results from  $\text{XeO}_3$  thermolysis via reactions (I) and (II), from reaction (XVI), and from radical recombination reactions (VII) and (VIII). Only at comparatively high reactant concentrations do reactions (VII) and (VIII) yield  $\text{H}_2\text{O}_2$  in amounts sufficient for the autoacceleration regime to take place. Hydrogen peroxide participates in the generation of  $\cdot\text{OH}$  and  $\text{HO}_2^\cdot$  radicals:



Therefore, along with reactions (IX)–(XII), reactions (III), (XVIII), and (XIX) also initiate new chains. As a consequence, the  $\cdot\text{OH}$  and  $\text{HO}_2^\cdot$  concentrations in the solution increase and, accordingly, the oxidation of both U(IV) and U(V) is accelerated. The CL intensity depends on the  $\text{UO}_2^{2+}$  and  $\cdot\text{OH}$  formation rates in the solution because the CL emitter excitation step is reaction (XV). The process becomes avalanchelike, and the reaction rate increases rapidly. Accordingly, the CL intensity grows and it reaches its maximum at the instant the  $\cdot\text{OH}$  generation rate exceeds the rate of  $\text{UO}_2^{2+}$  formation by U(IV) oxidation.

The inhibiting effect of silver ions on U(IV) oxidation is an indirect argument in favor of the participation of the  $\cdot\text{OH}$  and  $\text{HO}_2^\cdot$  radicals in the chemiluminescent reaction examined. The introduction of  $\text{AgNO}_3$  ( $10^{-6}\ \text{mol/l}$ ) into a  $0.1\ \text{M}\ \text{HClO}_4$  solution containing  $1 \times 10^{-5}\ \text{mol/l}$  U(IV) and  $5 \times 10^{-5}\ \text{mol/l}$   $\text{XeO}_3$  causes the CL intensity to decrease rapidly by a factor of several times. This is accompanied by a decrease in the rate constant of the chemiluminescent reaction (see Fig. 5, curve 2; the  $\text{AgNO}_3$  introduction point is indicated by an arrow). For comparison, Fig. 5 shows the time trace of the CL intensity for the reaction between U(IV) and  $\text{XeO}_3$  in a solution containing no  $\text{Ag}^+$  (curve 1). By reducing the solution temperature and the concentration of the oxidizer (added in excess), it is possible to

establish conditions under which the CL decay will obey an exponential law. The decreases in the CL intensity and in the CL decay rate are even larger in the presence of  $10^{-5}\ \text{mol/l}$   $\text{AgNO}_3$  added to the solution before U(IV) introduction (Fig. 5, curve 3). The rapid decrease of the luminance in the presence of  $\text{Ag}^+$  can be due to the decrease in the concentrations of  $\text{UO}_2^{2+}$  and  $\cdot\text{OH}$  caused by reactions (XX) and (XXI) because it is believed that these radicals are involved in the uranyl ion excitation step.



The  $\text{Ag}^+$  ions not only reduce the rate constant of the chemiluminescent reaction by trapping chain carriers, but also reduce  $\eta_{\text{CL}}$  by a factor of 2.7 ( $\eta_{\text{CL}}$  is  $1.2 \times 10^{-5}$  in the absence of silver ions and  $4.5 \times 10^{-6}$  at  $[\text{AgNO}_3] = 10^{-5}\ \text{mol/l}$ ). This effect is likely due to the fact that the silver ion is an efficient trap for the  $\cdot\text{OH}$  radical:  $k_{\text{XX}} = 6 \times 10^9\ \text{l mol}^{-1}\ \text{s}^{-1}$  at pH 5 [14]. When the interaction between U(IV) and  $\text{XeO}_3$  takes place in the presence of  $\text{Ag}^+$ , a decrease in the  $\cdot\text{OH}$  concentration because of reaction (XX), which is in competition with the chemiluminescent step (XV), can raise the contribution from the radiationless pathway of the reaction versus the luminescent pathway and thereby diminish the CL yield.

Thus, a critical phenomenon rare for liquid-phase radical chain processes is observed in the luminescent oxidation of U(IV) with xenon trioxide: a comparative small increase in the reactant concentrations causes the process to pass from the quasi-steady-state regime to autoacceleration.

## ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (grant no. 05-03-32285), a grant from the President of the Russian Federation (NSh 5486.2006.3), and a grant from the Department of Chemistry and Materials Science of the Russian Academy of Sciences (no. 1 OKh).

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