Brief Communications

Strong effect of a solid surface on a liquid-phase radical chain chemiluminescence reaction. Oxidation of U^{IV} by dioxygen

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The reaction of uranium(IV) with O_2 in aqueous solutions of $HClO_4$ is accompanied by chemiluminescence (CL). The CL intensity and the reaction kinetics are appreciably affected by introduction of the glass beads with a radius of 1 mm. In the presence of 1600 beads (the surface area of the glass is 200 cm^2), the yield of CL decreases 32-fold. The effect of the solid surface on the kinetic and chemiluminescence parameters of the liquid-phase radical chain reaction is due to the increased role of chain termination upon heterogeneous decay of the $HO_2^{\cdot}$ and $^{\cdot}OH$ radicals.

Key words: chemiluminescence, kinetics, glass, uranium(IV), uranyl ion, oxygen, $HO_2^{\cdot}$ and $^{\cdot}OH$ radicals.

The luminescence intensity in chemiluminescence processes such as heterogeneous decomposition of ozone[1] or hydrolytic reduction of XeF_2[2] increases proportionally to the surface area of the reaction vessel because this increases the number of radical species whose reactions are accompanied by chemiluminescence. However, heterogeneous decay of radicals on the liquid—solid interface is expected to decrease the rate of a radical chain liquid-phase reaction and, hence, to depress chemiluminescence (CL). When studying the chemiluminescence stage of the oxidation of uranium(IV) by dioxygen, we found that the reaction kinetics and the efficiency of transformation of the energy of chemical reaction into light energy depend appreciably on the surface area of the glass washed by the solution.

Experimental

The equipment for recording the CL and the procedures for purification of the reactants and preparation of solutions have been described previously.[3] Experiments on the study of the CL that accompanies the reaction of U^{4+} with O_2 in the presence of glass were carried out using a thin-wall (wall thickness 38 mm) polytetrafluoroethylene (Teflon F-4D) reactor containing 10 mL of doubly distilled water and a particular number (200, 400, 800, 1600, and 3470) of glass beads (R = 1 mm). A solution ($2.8 \cdot 10^{-2}$ mol L^{-1}) of $U(ClO_4)_4$ (0.01 mL) in $HClO_4$ (1 mol L^{-1}) was added to the reactor and the mixture was quickly stirred. The CL was recorded at ambient temperature 10—15 s after the beginning of the reaction.

The CL spectrum was studied using glass light filters with sharp transmission boundaries. The fact that the spectral region

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of CL coincides with that of the photoluminescence of uranyl ion in $HClO_4$ solutions indicates that $(UO_2^{2+})^*$ is the CL emitter.

Results and Discussion

The oxidation of U^{4+} by dioxygen is a radical chain process. Its mechanism includes the formation of a pentavalent uranium ion (UO_2^+) and the $HO_2^{\cdot}$ radical at the initiation stage, UO_2^+, H_2O_2, and $^{\cdot}OH$ radicals in the chain propagation processes, and uranyl ion in the chain termination step.[4] The time variation of the intensity of CL of this reaction is described by a curve with a maximum (Fig. 1, curve *1*). Under the conditions of our experiments, the reactions of UO_2^+ with O_2 and UO_2^+ with H_2O_2 were not accompanied by light emission. In our opinion, the electronically excited uranyl ion is formed upon the transfer of an electron from UO_2^+ to $^{\cdot}OH$:

$$UO_2^+ + {}^{\cdot}OH + H^+ \longrightarrow H_2O + (UO_2^{2+})^* \longrightarrow$$

$$\longrightarrow UO_2^{2+} + h\nu. \qquad (1)$$

The possible contribution of the luminescence that accompanies oxidation of UO_2^+ with an $HO_2^{\cdot}$ radical to the observed CL is fairly low because the rate of this process[5] is several orders of magnitude lower than the rate of reaction (1).[6]

The kinetics of liquid-phase reactions under standard conditions are slightly affected by heterogeneous decay of radicals. However, if the ratio of the surface area of the reactor to its volume is not very low and the probability of the decay of radicals on the solid surface (γ) is sufficiently high, heterogeneous chain decay processes can noticeably affect the reaction kinetics.

We found that the introduction of glass beads with a total surface area (S_g) equal to 25, 50, 100, 200, and 436 cm^2 into a solution of $HClO_4$ (0.001 mol L^{-1}) containing U^{4+} and O_2 causes a substantial decrease in the maximum CL intensity (I_{max}) and shortens the time required to attain I_{max} (t_{max}) (see Fig. 1, curves *2*—*6*, respectively).

The presence of glass in a solution has a substantial influence on both the kinetic and the chemiluminescence parameters of the reaction: the values of t_{max} and the yield of CL (η_{CL}) decrease exponentially as the surface area of the glass increases from 0 to 100 cm^2 (Fig. 2, curves *1* and *2*). The I_{max} value depends on S_g (Fig. 2, curve *3*) according to a more complex pattern. The data shown in Fig. 2 make it possible to estimate quantitatively the effect observed. Thus upon introduction of 1600 beads (S_g = 200 cm^2), the η_{CL} value decreases 32-fold (from $2.8 \cdot 10^{-7}$ to $8.9 \cdot 10^{-9}$), I_{max} decreases 20-fold (from $1 \cdot 10^8$ to $5 \cdot 10^6$ photons s^{-1}), and t_{max} decreases by an order of magnitude (from 10 to 1 min).

We believe that the discovered effect is due to the substantial increase in the fraction of the $^{\cdot}OH$ and $HO_2^{\cdot}$ radicals that are destroyed on contact with the solid

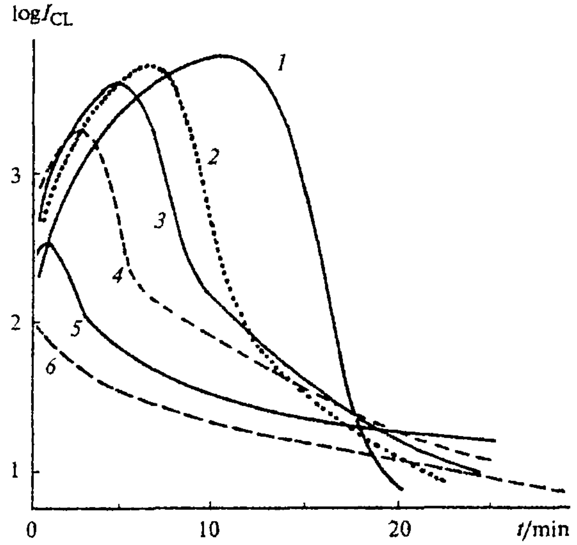

Fig. 1. Time dependence of the chemiluminescence (I_{CL}) during the reaction of U^{4+} with O_2 in the presence of glass beads with a total surface area (S_g) of 0 (*1*), 25 (*2*), 50 (*3*), 100 (*4*), 200 (*5*), and 436 cm^2 (*6*). $[U^{4+}]_0 = 2.8 \cdot 10^{-5}$ mol L^{-1}; $[HClO_4]$ = 0.001 mol L^{-1}; $[O_2] = 2.4 \cdot 10^{-4}$ mol L^{-1}; T = 291 K.

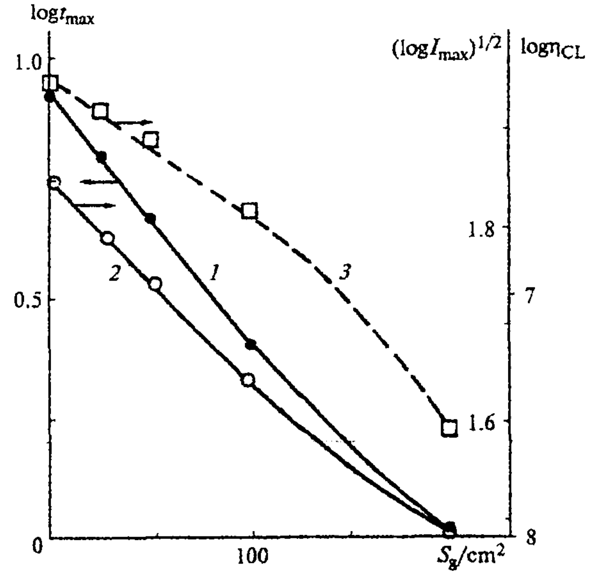

Fig. 2. Time (t_{max}) required to attain the maximum chemiluminescence intensity (I_{max}) (*1*), chemiluminescence yield (η_{CL}) (*2*), and the maximum chemiluminescence intensity (I_{max}) (*3*) *vs* the total surface area (S_g) of the glass beads washed with the solution. $[HClO_4] = 0.001$ mol L^{-1}; $[U^{4+}]_0 = 2.8 \cdot 10^{-5}$ mol L^{-1}; $[O_2] = 2.4 \cdot 10^{-4}$ mol L^{-1}; T = 291 K.

surface. The probabilities of decay (γ) of the $HO_2^{\cdot}$ and $^{\cdot}OH$ radicals getting on the Teflon or quartz surface from the gas phase at 300 K have been measured experimentally.[7,8] In the case of the $HO_2^{\cdot}$ radical, they were found[7] to be $(1.2-2.4) \cdot 10^{-4}$ and $(5.7-11.4) \cdot 10^{-4}$, respectively, and those for the $^{\cdot}OH$ radical[8] are $0.3 \cdot 10^{-3}$ and $3 \cdot 10^{-3}$, respectively. It follows from these γ values that the probability of the decay upon collision with the quartz surface is 5 times greater for $HO_2^{\cdot}$ and 10 times greater for $^{\cdot}OH$ than the corresponding values for the interaction with Teflon. It can be assumed that the γ values do not change much on passing from the gas phase to a solution in $HClO_4$ (0.001 mol L^{-1}) and the probability of the decay of radicals on glass is not lower than that on quartz. In our experiments, the surface area of the Teflon reactor washed by the solution varied from 22 to 37 cm^2 and the total surface area of the glass ranged from 25 to 436 cm^2. Hence, in the presence of the glass, the number of radicals that decay on the solid surface increases by one or two orders of magnitude, which evidently affects the reaction kinetics.

A specific feature of the reaction kinetics in the case where a part of the solution occurs in the inter-bead space and the rest occurs in the glass-free layer is the presence of an inflection on the plot for the CL intensity *vs* time (see Fig. 1, curves *2*—*5*). It can be suggested that without stirring of the solution, which could be either mechanical or due to convection, the bell-shaped section of the kinetic curve from the beginning of the reaction up to the inflection corresponds to the reaction occurring in the solution layer covering the beads and the slower attenuation of the luminescence intensity is associated with the processes in the inter-bead space, cut into cells with a characteristic size of 0.155 mm. The limiting situations, *i.e.*, a reactor without glass and a reactor in which the solution is entirely contained in the cells between the beads, are shown by kinetic curves *1* and *6*, respectively (see Fig. 1). In the latter case, the luminescence peak is totally missing and the yield of CL (η_{CL}) is 65 times lower than η_{CL} in a reactor without glass. Apparently, in a cell with small dimensions (compared to the thickness of the glass-free layer of the solution), the lifetime of radicals becomes shorter and their concentration, which influences the rate of development of the chain process, decreases.

We believe that such a so pronounced decrease in the yield of CL in the presence of glass in a solution is due to the essential change in the ratio of radiative and radiationless reaction pathways toward the latter. In fact, the probability of decay of the $^{\cdot}OH$ radicals on the quartz surface is at least 10 times as great as that for the $HO_2^{\cdot}$ radicals (see the γ values presented above). Thus, the relative contribution of dark reactions (involving the $HO_2^{\cdot}$ radicals) to the overall oxidation of U^{4+} to UO_2^{2+} is greater than the contribution of the chemiluminescence step of electron transfer from the UO_2^{+} ion to the $^{\cdot}OH$ radical.

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