Chemiluminescence in the reduction of XeO_3 by europium(II)

A. D. Karavaev and V. P. Kazakov*

*Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: 007 (347 2) 35 6066*

Chemiluminescence has been observed in the reduction of perchloric aqueous solutions of XeO_3 with Eu^{2+} ions. Fast (several seconds) consumption of Eu^{II} occurs when the ratio of the initial concentrations of the reactants $[Eu^{2+}]_0 : [XeO_3]_0 < 6$; however, the chemiluminescence remains sufficiently bright and prolonged (up to ~10 min after nearly complete oxidation of Eu^{II} to Eu^{III}). The assumption was made that intermediates in the reduction of XeO_3 participate in the chemiluminescent stages of the process.

Key words: chemiluminescence; kinetics; xenon trioxide, europium(II,III) ions.

The development of the chemistry of the noble gases has motivated the synthesis of a large number of simple and complex compounds, in which atoms of these elements occur in various valent states.[1—3] It is of interest to investigate the oxidation-reduction reactions of xenon compounds in aqueous solutions, where multistep processes involving labile intermediates proceed. It was shown previously that the oxidation of uranium(IV) by xenon trioxide, whose aqueous solutions are fairly stable, is accompanied by bright chemiluminescence (CL).[4—6] In this work, the chemiluminescence found in the reaction of XeO_3 with another reducing agent, europium(II), is reported.

Experimental

The measurements were carried out on a chemiluminescent installation with spectral sensitivity in the region from 320 to 650 nm (the light equivalent of the inherent noise ~10^4 photon s^{-1}). The solutions of the reagents were mixed for 1—1.5 s in a glass flat-bottomed cuvette placed over the photocathode of a FEU-97 photoelectronic multiplier in a light-tight chamber. The reaction mixture was stirred with a glass stirrer. The cuvette was thermostated at 298.0±0.2 K. The experiments were carried out under an argon atmosphere. Bidistilled water was used to prepare the solutions. The perchloric acid was purified by distillation at a reduced pressure. Perchloric solutions of Eu^{II} were prepared from $EuCO_3$ obtained by reduction of Eu^{III} on amalgamated zinc. To determine the concentration of Eu^{II}, its reaction with Fe^{III} was used. The equivalent amount of Fe^{II} formed was found following a standard photometrical procedure by using *o*-phenanthroline. Solutions of XeO_3 were obtained by dissolution of sodium perxenate[3] in 1 *M* $HClO_4$; XeO_3 concentration was then determined by iodometric methods. The perchloric solutions of Eu^{III} and U^{VI} were obtained from Eu_2O_3 and UO_3. The spectral region of the glow was recorded by cut-off light filters. The concentration of $HClO_4$ in the experiments was 1 mol L^{-1}.

Results and Discussion

The shape of the kinetic curve of chemiluminescence depends on the ratio of the initial concentrations of the reactants $\alpha = [Eu^{II}]_0/[XeO_3]_0$ ($\alpha = 6$ coresponds to the strict stoichiometric ratio). In excess Eu^{II} ($\alpha > 12$), the chemiluminescence ceases in less than 30 s (Fig. 1). The mixing of the reactants is accompanied by a "flash" of the glow, then a fast drop in the CL intensity (*I*). Since in this case the CL kinetics reflects the dynamics of the reduction of XeO_3 by the Eu^{II} ions (mixing Eu^{III} and XeO_3 solutions is not accompanied by the glow), one can assume that this reaction is fast and is completed to a large extent during the mixing of the solutions (1—2 s). The previously investigated[7] analogous reaction of XeO_3 with excess Ti^{III} (which is a one-electron reducing agent with a similar redox potential), is also completed in 30 s.

However, the chemiluminescence is observed for a much longer time (to ~10 min, Fig. 2) if the reaction is carried out in excess XeO_3 ($\alpha < 6$). In this case, a "flash" of the glow (associated with the oxidation of Eu^{II}) is also recorded at first, but one or two maxima then appear on the kinetic curve of chemiluminescence, and there is a clearly defined induction period between the initial "flash" and the subsequent increase in *I*.

To elucidate the nature of the "long-lived" chemiluminescence, one needs to estimate the time of the Eu^{II} consumption in the solution of XeO_3 using an independent procedure. Because of the great difficulties in applying titrometric or spectrophotometric (due to the overlap of the absorption bands of the reactants) techniques, we used the chemiluminescent titration of europium(II) by uranium(VI) immediately in the reaction mixture. This technique is based on the fact that the UO_2^{2+} ions are very quickly reduced to UO_2^{+} by europium(II) (the rate constant of this reaction[8] $k =$

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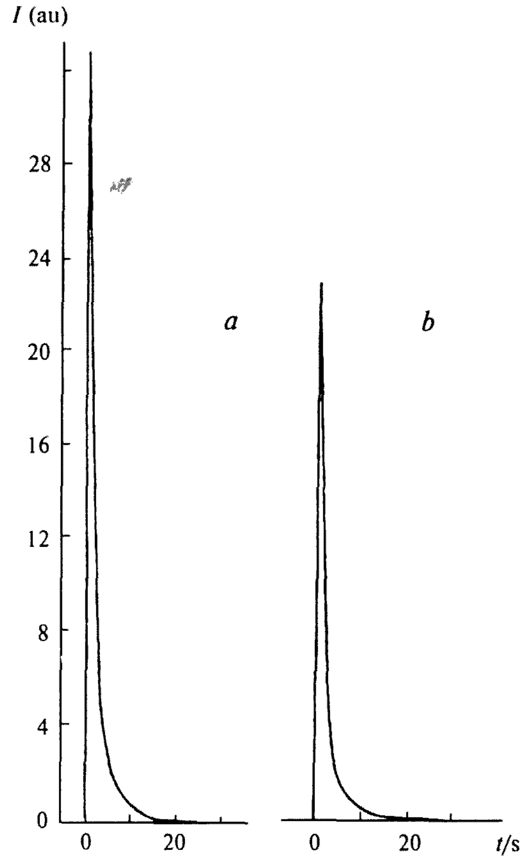

Fig. 1. The kinetics of CL at $\alpha > 12$. *a*. $[Eu^{2+}]_0 = 2.0 \cdot 10^{-3}$, $[XeO_3]_0 = 9.6 \cdot 10^{-5}$ mol L^{-1}, $\alpha = 20.8$; *b*. $[Eu^{2+}]_0 = 2.0 \cdot 10^{-3}$, $[XeO_3]_0 = 4.8 \cdot 10^{-5}$ mol L^{-1}, $\alpha = 41.7$.

$1.68 \cdot 10^4$ L mol^{-1} s^{-1}). Uranium(v), in its turn, is oxidized under the action of XeO_3 and disproportionates to form U^{IV}, which again enters the reaction with XeO_3. Oxidation of the low-valent forms of uranium is accompanied by bright chemiluminescence[4—6] whose intensity is 3—4 orders of magnitude higher than the brightness of the glow in the course of the interaction between Eu^{II} and XeO_3. As is shown in Fig. 3, there is a sharp rise in I after the introduction of uranyl into the reaction mixture several seconds after the reaction starts. Only a small increase in I (by a factor of 5—7 at uranyl concentrations of $(3—8) \cdot 10^{-3}$ mol L^{-1}) with no essential change in the kinetics of the chemiluminescence is recorded if U^{VI} is introduced 3 (or more) min after Eu^{II} is mixed with XeO_3. In this case, UO_2^{2+} only serves as a sensitizer of the chemiluminescent reactions that proceed after the consumption of Eu^{II}. The concentration of Eu^{II} in the reaction mixture can be estimated from a comparison of the total light of the chemiluminescence ($S = \int I dt$), obtained after the introduction of UO_2^{2+} with the total light of the calibrating experiments (in which first excess UO_2^{2+} was introduced into a solution with a known concentration of Eu^{II}, and then a solution of XeO_3 was added).

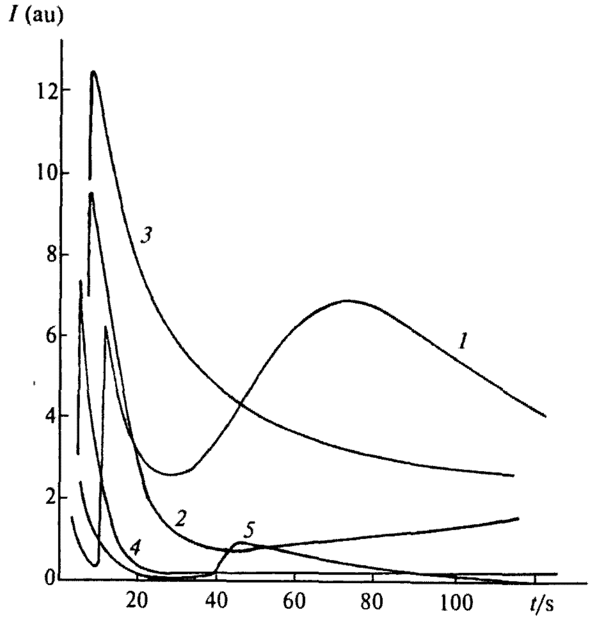

Fig. 2. The kinetics of CL at $0.9 < \alpha < 7$. $[Eu^{2+}]_0 = 2.0 \cdot 10^{-3}$, $[XeO_3]_0 = 3.8 \cdot 10^{-4}$ mol L^{-1}, $\alpha = 5.3$ (*1*); $[Eu^{2+}]_0 = 2.2 \cdot 10^{-3}$, $[XeO_3]_0 = 5.3 \cdot 10^{-4}$ mol L^{-1}, $\alpha = 4.2$ (*2*); $[Eu^{2+}]_0 = 2.2 \cdot 10^{-4}$, $[XeO_3]_0 = 9.8 \cdot 10^{-5}$ mol L^{-1}, $\alpha = 3.6$ (*3*); $[Eu^{2+}]_0 = 4.0 \cdot 10^{-4}$, $[XeO_3]_0 = 4.6 \cdot 10^{-4}$ mol L^{-1}, $\alpha = 0.9$ (*4*); $[Eu^{2+}]_0 = 2.0 \cdot 10^{-3}$, $[XeO_3]_0 = 2.9 \cdot 10^{-4}$ mol L^{-1}, $\alpha = 6.9$ (*5*). For clarity, the initial portions of the curves are not shown.

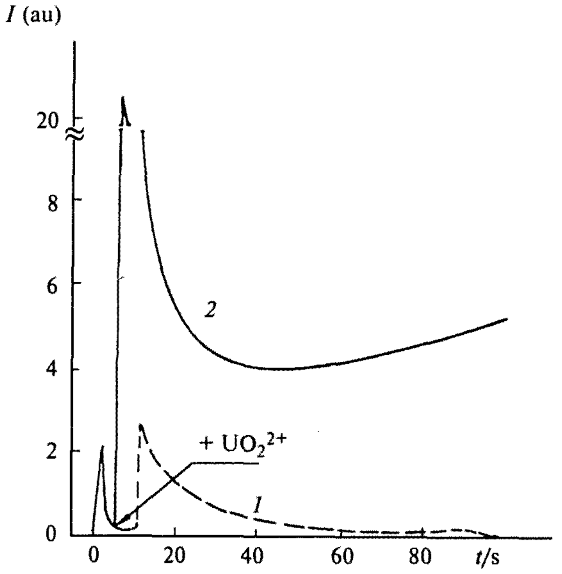

Fig. 3. The kinetics of chemiluminescence after the introduction of uranyl ions into solutions of Eu^{2+} and XeO_3. *1*, without UO_2^{2+} (*I* enlarged by a factor of 10), *2*, after introduction of uranyl. $[XeO_3]_0 = 1.8 \cdot 10^{-4}$ mol L^{-1}, $[Eu^{2+}]_0 = 8.2 \cdot 10^{-4}$ mol L^{-1}, $[UO_2^{2+}] = 3.7 \cdot 10^{-3}$ mol L^{-1}.

The experiments showed that Eu^{II} is very rapidly consumed in a solution of XeO_3. Thus, at $[XeO_3]_0 = 1.9 \cdot 10^{-4}$ mol L^{-1} and $[Eu^{II}]_0 = 8.4 \cdot 10^{-4}$ mol L^{-1}

(α = 4.4), the concentration of Eu^{II} is less than 1% of its initial value 5 s after the start of the reaction, and 1 min later it further decreases by two orders of magnitude.

Thus, it is believed that the "long-lived" chemiluminescence at $\alpha < 6$ occurs in reactions of intermediates of XeO_3 reduction. This is also confirmed by the chemiluminescence we observed in the reduction of XeO_3 by Fe^{2+} ions — the Fe^{3+} ions formed have no luminescence in solutions. In the literature,[1—3,9] XeO, XeO_2, and $HXeO_3$ formed were assumed to be such intermediate products (they are considered to be unstable and incapable of accumulation in solution). In addition, traces of H_2O_2, which is the only stable intermediate in the reduction of XeO_3, have been recorded.[3,7,8]

It is known that the reaction of XeO_3 with H_2O_2 is chemiluminescent (the red and infrared radiations are observed in sulfuric solutions, the latter being assigned to singlet oxygen), and the CL brightness sharply increases in the presence of uranyl ions.[10] However, the rate of this reaction is not high in perchloric solutions (k = 37 L mol^{-1} min^{-1} in 1 M $HClO_4$ with excess XeO_3 [11]), and at the concentrations of XeO_3 (~10^{-4} mol L^{-1}) we used, the characteristic time of the reaction is several hours, which far exceeds the duration of the chemiluminescence we observed. In addition, the unusual kinetics of the "long-lived" chemiluminescence in the reaction of Eu^{II} with XeO_3 (with one or two maxima) does not allow us to restrict our consideration to the reaction of XeO_3 with H_2O_2. It is likely that in the course of the reduction of XeO_3, xenon compounds are obtained in which the xenon is in intermediate oxidation states. The lifetimes of those compounds in an acidic aqueous solution are several minutes. This is supported by the observed[12] progressive increase in the electrode potential (from 1.0 to 1.2 V) in the initial portion of the titration curve of a solution of XeO_3 by a solution of Fe^{II}. This can be explained by the formation of xenon-containing intermediates with stronger oxidative properties, which can exist in solution for several minutes. It is also not improbable that free-radical particles of the $^{\cdot}ClO_3$ type are generated in side reactions with the perchloric ions. Previously, the chemiluminescence in some oxidizing reactions of ozone in the perchloric medium has been associated with these $^{\cdot}ClO_3$ type particles.[5] Further investigations are needed to elucidate this question.

Apart from the basic glow in the red region (at $\lambda \geq$ 580 nm), an additional blue-green component ($\lambda \approx$ 420—510 nm) was observed in the spectrum of the "long-lived" chemiluminescence. The appearance of the red component can be related to sensitizing of the light stages of the process by the Eu^{III} ions formed. To verify this assumption, Eu^{3+} ions were introduced into the Eu^{II}—XeO_3 system at a 25—50-fold excess relative to the content of the starting Eu^{II}. In this case I was only found to increase by a factor of 1.5—2.5. Therefore, sensitizing of the "long-lived" chemiluminescence by the europium(III) formed directly in the course of the process is not high. A probable emitter of the red glow is electron-excited oxygen (molecular or monatomic), for which the corresponding bands of luminescence are known.[13] The nature of the emitters of the blue-green component of the glow is not clear. It is possible that they are xenon compounds, in which xenon is in intermediate oxidation states (such as XeO,), for which green luminescence in the gas phase and in solid matrices is known.[14]

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