Generation of an oscillating chemical reaction in a heterogeneous system by the oxidation of an alkaline solution of luminol with sodium(VI) ferrate in the presence of copper ions

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Chemiluminescence accompanying the oxidation of 3-aminophthalhydrazide (luminol) with sodium ferrate (VI) in an alkaline solution is studied. The powerful initial light flash flaring up at the moment of mixing the reactants is followed by a continuous low-intensity luminescence in the heterogeneous system formed. The addition of Cu^{2+} ions during this period results in a new chemiluminescence flash with an oscillating character.

Key words: chemiluminescence, sodium ferrate(VI), luminol, oscillating reaction, copper ions.

We have previously[1] observed a strong chemiluminescence (CL) accompanying the oxidation of luminol with the FeO_4^{2-} anion in an aqueous solution of alkali. The reduction of Fe^{VI} in an alkaline solution affords Fe^{V} and Fe^{IV} compounds capable of oxidizing luminol and other oxidants, *viz.*, O_2^{2-}, O_2, H_2O_2, and $OH^{\bullet}$ and $HO_2^{\bullet}$ radicals.[2,3] The resulting products of Fe^{VI} reduction are Fe^{III} hydroxo complexes with a developed surface, which participates in the chemiluminescence reaction.[4] In this work we studied the CL and the influence of additives of d-metals, in particular, Cu^{2+} ions, on its intensity and time relation.

Experimental

"White" luminol and Na_4FeO_5 obtained by the described procedures[5,6] were used. Solutions of KOH and $CuCl_2$ were prepared from commercially available substances (reagent grade) and bidistilled water.

Chemiluminescence spectra were recorded on a KSVU-1 universal spectral-calculation complex (LOMO, St. Petersburg) supplied with an MDR-2 monochromator and an FEU-100 photoelectron amplifier. The main CL band in the 350—530 nm region has a maximum at 428 nm.

Luminol ($2.5 \cdot 10^{-4}$ mol L^{-1}) dissolved in a 0.02 *M* solution of KOH (pH 12.5) was added to a weighed sample of Na_4FeO_5, and the mixture was stirred with a speed of 600 rpm. (In aqueous solutions the ferrate(VI) ion exists as FeO_4^{2-}.)

Results and Discussion

An intense luminescence arose on mixing the reactants and stopped sharply after several seconds. However, the noticeable radiation of the heterogeneous mixture that formed (mixture **I**) continued during tens of minutes. For a weighed Na_4FeO_5 sample of 1—3 mg and a volume of the luminol solution of ~10 mL, the luminescence after the primary flash remained almost unchanged for ~20 min (Fig. 1, curve *1*).

The addition of the d-metal (Cd^{2+}, Ni^{2+}, or Co^{2+}) into heterogeneous mixture **I**, which luminesced with a constant and low intensity, initiated a new light flash with a duration of 1—1.5 min, and the luminescence intensity returned to the constant value. The intensity of the flash depends on the amount of the added metal (see Fig. 1, curve *2*).

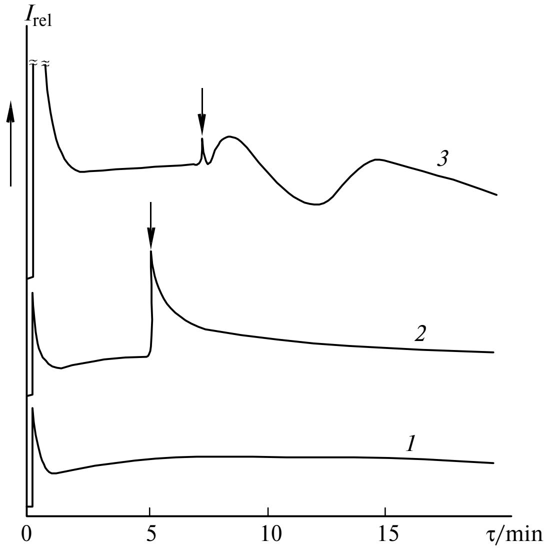

Fig. 1. Relative intensity of chemiluminescence (I_{rel}) as a function of time (τ) with d-metal additives in the system (moments of addition are shown by arrows): *1*, without d-metal additive; *2*, Ni^{2+} ($3 \cdot 10^{-6}$ mol L^{-1}); and *3*, Cu^{2+} ($1 \cdot 10^{-5}$ mol L^{-1}).

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When $CuCl_2$ was added to mixture **I**, the time relation of CL had a different character. Curve *3* in Fig. 1 shows the typical time relation of CL. The oscillating character of CL with an elongating oscillation period is associated, perhaps, with the formation of two redox pairs (Cu^{II}—Cu^{I} and O^{II}—O^{I}) in the system and the appearance of conditions for the reversible redox reaction between these forms. A similar reason for the appearance of stable oscillations of concentrations of heterovalent copper forms was found for solid coordination oxides, *e.g.*, $YBa_2Cu_3O_{7-x}$ or $LaBa_2Cu_3O_{7-x}$.[7] The appearance of superconductivity in these solid oxides is ascribed to this reversible redox reaction.

Two distinctive features can be emphasized: the possibility of comparatively easy formation of Cu^+ ions when Cu^{2+} ions are introduced into mixture **I** and the probability that the surface of the solid phase (perhaps, colloidal) formed by the Fe^{III} and Fe^{II} hydroxo forms is involved in the chemiluminescence reaction. It is known that in the presence of reducing agents, for example, sulfide, sulfite, or selenite ions, the ferrate(VI) ion is rapidly reduced in an alkaline medium to Fe^{II}, and only after this are the resulting Fe^{III} hydroxo forms formed.[2,8,9] The reduction of the FeO_4^{2-} ion with luminol during the emerging chain radical processes results in CL (the first maxima followed by a plateau in curves *1—3*, Fig. 1).

An approximate scheme of the process under study can be described as follows. In a strongly alkaline medium (pH > 10), the FeO_4^{2-} ion is reduced by water to Fe^{IV} [10]:

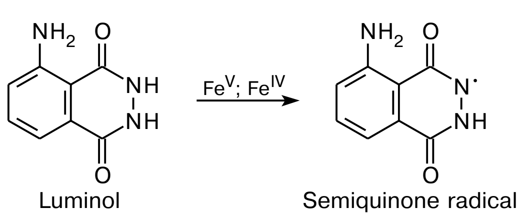
$$FeO_4^{2-} + H_2O + OH^- \rightarrow H_2O_2 + HFeO_4^{3-}. \quad (1)$$

In the presence of strong reducing agents in an alkaline medium, the FeO_4^{2-} ion is rapidly reduced to Fe^{II}.[2,8,9] Subsequent reactions of the $Fe(OH)_2$ that formed produce highly reactive compounds of Fe^{V} and Fe^{IV} in the solution and reactions brought about these compounds, for example,

$$HFeO_4^{-} + Fe(OH)_2 + OH^- \rightarrow HFeO_4^{2-} + Fe(OH)_3, \quad (2)$$

$$HFeO_4^{2-} + H_2O \rightarrow Fe(OH)_3 + O_2^{2-}. \quad (3)$$

The formed Fe^{V} and Fe^{IV} compounds oxidize reducing agents present in the solution, *e.g.*, H_2S and HCN, to the free radicals $HS^{\bullet}$ and $CN^{\bullet}$, respectively. Semiquinone radicals can be formed *via* a similar mechanism in a complex system, which appears when the FeO_4^{2-} ion is added to an alkaline solution of luminol



(4)

and/or luminol peroxide generated by the $HO_2^{\bullet}$ radical, which then decomposes and emits light.[11]

Along with the reduction of Fe^{VI} to Fe^{II}, Cu^{II} can be reduced to Cu^{I} by the same radicals. The Cu^{2+} ions introduced into the heterogeneous mixture **I** are most likely hydrolyzed immediately, sorbed on the surface of suspended Fe^{III} oxide-hydroxide, and produce the secondary flash of luminescence. Their slow reduction with organic radicals followed by secondary oxidation with peroxide radicals on the surface of the suspended phase determine the oscillating character of CL with an elongating oscillation period. We believe that the Cu^{II} compounds enhance CL, whereas the Cu^{I} compounds quench it.

These assumptions are confirmed by the character of CL observed when silver ions are added to system **I**: at Ag^+ concentrations of $1 \cdot 10^{-6}$—$1 \cdot 10^{-5}$ mol L^{-1} the CL intensity first strongly increases, and the CL signal forms a broad flat bell-shaped maximum and then smoothly disappears within ~20—30 min, but does not reach a plateau as in curve *2* (Fig. 1). At Ag^+ concentrations $\geq 1 \cdot 10^{-4}$ mol L^{-1} CL is quenched (the formation of a sharp minimum in the plot of CL *vs.* time); then its intensity increases rapidly to a flat maximum, and finally CL smoothly disappears as at smaller additives of silver. This character of change in the CL intensity may be due to the oxidation of Ag^{I} to Ag^{II} on the surface of the hydroxo complexes. This oxidation is prolonged in time, resulting in a broad maximum in the time plot of the CL intensity. Then the CL intensity gradually decreases to zero due to the reduction of Ag^{II} to Ag^{I} instead of reaching a plateau, which was always observed when Cd^{2+}, Ni^{2+}, and Co^{2+} cations were added.

The obtained results explain the oscillating character of luminescence flaring up during luminol oxidation with sodium ferrate(VI) in an alkaline medium in the presence of Cu^{2+} cations.

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