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Features of Chemiluminescence Arising in Oxidation of Luminol with Ferrate(VI) Ions in Alkaline Solutions

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Abstract—Mixing of solid sodium ferrate(VI) and luminol solution in 0.02 M KOH gives rise to a chemiluminescence flash with the peak intensity h_1 followed by a weak luminescence for ~20 min with approximately constant intensity. The addition of *d*-metal ions (Cd^{2+}, Ag^{+}, Ni^{2+}, or Co^{2+}) to the mixture in this period gives rise to a new flash with the intensity h_2. The ratio h_2/h_1 is proportional to the concentration of the *d*-metal ions. The value of h_2 is most strongly affected by Sythofloc EM 6159 cationic flocculant and Triton X-100 neutral surfactant.

We observed a strong chemiluminescence accompanying oxidation of luminol (3-aminophthalhydrazide) with sodium ferrate(VI) in alkaline solution and reported some of its features in [1]. These features were studied in more detail in the present work.

It is known that luminol and hydrogen peroxide purified to remove heavy metals react in alkaline solutions without a chemiluminescence which is initiated by ions of several *d* metals: Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Mn^{2+} [2]. This chemiluminescence is assumed to arise when a radical-chain mechanism is realized, which can involve semiquinone, $HO_2^{\bullet}$, and other radicals formed in the reaction of a *d*-metal compound with H_2O_2 or luminol. Usually the chemiluminescence is observed in the pH range 10–12, and it is assumed to take place in all the cases in a heterogeneous medium, as even at minimum concentrations of a *d* metal introduced in solution (10^{-7}–10^{-8} M) the solubility product of the corresponding hydroxide is exceeded by several orders of magnitude [3, 4].

It was shown in [5] that a chemiluminescence flash accompanying the reaction of luminol and H_2O_2 in the presence of an iron(III) complex with acetylacetone is induced by finely divided Fe(III) hydroxide formed by hydrolysis of this complex at pH 10–12.

Let us show that the oxidation of luminol with ferrate(VI) ions in an alkaline aqueous solution should result in a chemiluminescence.

Ferrate(VI) ion has a high redox potential dependent on pH of a medium [6].

$$FeO_4^{2-} + 8H^+ + 3e \rightarrow Fe^{3+} + 4H_2O,\quad E_0\ +2.20\ \text{V}, \quad (1)$$

$$FeO_4^{2-} + 4H_2O + 3e \rightarrow Fe(OH)_3 + 5OH^-,\quad E_0\ +0.72\ \text{V}. \quad (2)$$

The mechanism of ferrate(VI) reduction to Fe(III) hydroxide in an alkaline medium, which was found in [5] to induce a chemiluminescence, includes intermediate stages of formation of such active oxidants as Fe(V) and Fe(IV) compounds, and also can result in the formation of other oxidants: O_2^{2-}, O_2, hydrogen peroxide, and subsequently $OH^{\bullet}$ and $HO_2^{\bullet}$ radicals accompanying H_2O_2. In alkaline aqueous ferrate solution at pH < 9 the sequence of reactions (3)–(5) takes place [7].

$$FeO_4^{2-} + H_2O \rightleftarrows HFeO_4^- + OH^-, \quad (3)$$

$$HFeO_4^- + FeO_4^{2-} \rightleftarrows Fe_2O_7^{2-} + OH^-, \quad (4)$$

$$Fe_2O_7^{2-} + 2H_2O \rightarrow O_2 + H_2FeO_4^- + H_2FeO_3^-. \quad (5)$$

In a strongly alkaline medium (pH > 10) ferrate(VI) is reduced to Fe(IV) according to scheme (6) [7].

$$FeO_4^{2-} + H_2O + OH^- \rightarrow H_2O_2 + HFeO_4^{3-}. \quad (6)$$

In the presence of strong reducing agents, e.g., sulfide, sulfite, or selenite ions, ferrate(VI) ions are rapidly reduced in alkaline solutions to Fe(II) [8–11], and the subsequent reactions of the resulting $Fe(OH)_2$ again generate extremely reactive Fe(V) and Fe(IV) compounds in solution, which gives rise to the following reactions.

$$HFeO_4^- + Fe(OH)_2 + OH^- \rightarrow HFeO_4^{2-} + Fe(OH)_3, \quad (7)$$

$$HFeO_4^{2-} + H_2O \rightarrow Fe(OH)_3 + O_2^{2-}. \quad (8)$$

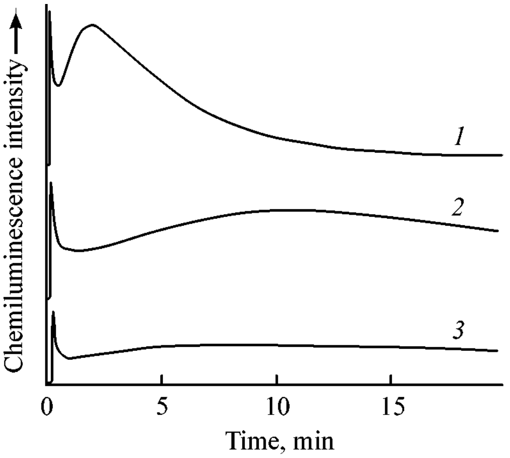
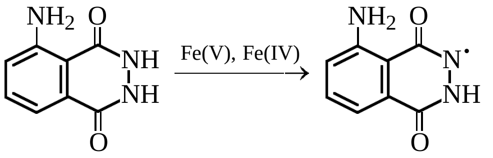


Fig. 1. Time dependence of chemiluminescence at various weighed portions of sodium ferrate(VI) added to 10 ml of aqueous alkaline solution of luminol (pH 12.3, concentration of luminol 2.5×10^{-4} M). Weighed portion, mg: (*1*) 2.1, (*2*) 0.5, and (*3*) 0.1.

The resulting Fe(V) and Fe(IV) compounds oxidize the reducing agents present in solution, e.g., H_2S and HCN, to the free radicals $HS^{\bullet}$ and $CN^{\bullet}$, respectively. When ferrate(VI) ions are added to an alkaline solution of luminol, semiquinone radicals can be formed by a similar mechanism (9), whose further transformations can be accompanied by emission, and/or luminol peroxides can be formed under the action of $HO_2^{\bullet}$ radicals with their subsequent decomposition and light emission [2].



(9)

It follows from the aforesaid that the oxidation of luminol with ferrate(VI) ions in alkaline medium should result in a chemiluminescence.

The aim of this work was to find optimal conditions for the excitation of such chemiluminescence and to elucidate the effect of certain *d*-metal ions added to already luminescent heterogeneous systems, and also the effect of some surfactants on the intensity and time dependence of the luminescence.

We will consider a signal recorded from a chemiluminescence flash arising on mixing a luminol solution with a weighed portion of ferrate as a reference signal and denote it as CL_0. Even in ~1 min the intensity of the CL_0 signal decreased to the level of CL_s and flattened out, remaining approximately constant for at least 20 min.

The shape of a time dependence of chemiluminescence in such “blank” experiments (without any additions) was a function of the ferrate portion. Three time dependences of the chemiluminescence intensity for different portions of sodium ferrate(VI) are shown in Fig. 1. At a constant volume of a standard luminol solution an increase in the weight of a sodium ferrate(VI) portion resulted in an increase in the chemiluminescence intensity and yield (an area under a curve), but for large ferrate portions the nature of the chemiluminescence became complicated. Time-extended dissolution of ferrate itself can be a possible reason for it. Therefore, in further experiments we used ferrate portions of 0.1–0.4 mg/ml (0.8–3 mg per an experiment) so that the chemiluminescence intensity changed according to curve *3* in Fig. 1.

Within 3–5 min after reaching a plateau 1 ml of solution of a *d*-metal salt of suitable concentration was introduced in a cell, and a change in the chemiluminescence intensity (analytical signal CL_0) was recorded.

In this work we studied the effect of additions of Cd^{2+}, Ag^{+}, Ni^{2+}, and Co^{2+} ions on the intensity of the chemiluminescence accompanying luminol oxidation by ferrate(VI) ions. For each experiment of this series we carried out also parallel experiments with a standard alkaline solution of luminol (pH 12.3, luminol concentration 2.5×10^{-4} M) and hydrogen peroxide as an oxidant (H_2O_2 concentration 2×10^{-3} M) at the same concentrations of *d*-metal ions. This concentration of H_2O_2 corresponds to the 1.3×10^{-3} M concentration of sodium ferrate(VI). Weighed portions of sodium ferrate(VI) (1–3 mg) used in the experiments were sufficient to create in solution concentrations close to those above-mentioned.

Introduction of Cd^{2+} or Ag^{+} ions into an aqueous alkaline solution of luminol and H_2O_2 (system I) did not excite a chemiluminescence at any concentrations of *d*-metal ions.

Introduction of Cd^{2+} ions into a heterogeneous system [aqueous alkaline solution of luminol + sodium ferrate(VI)] (system II) emitting light with a constant intensity CL_s resulted first in a sharp flash of chemiluminescence (measured signal CL_a) lasting for a few seconds and then in its return to the former value CL_s within 1–1.5 min. An increase in the Cd^{2+} concentration in solution increased the signal CL_a. Two typical experimental plots of chemiluminescence intensity as functions of time for two concentrations of Cd^{2+} ions in system II are given in Fig. 2.

Ratio of peak heights h_2/h_1 of analytical (CL_a) and reference (CL_0) chemiluminescence signals in system II on addition of *d*-metal ions

Cd^{2+} ($CdSO_4$)		Ag^+ ($AgNO_3$)		Co^{2+} ($CoSO_4$)		Ni^{2+} ($NiSO_4$)	
C, M	h_2/h_1[a] (average)	*C*, M	h_2/h_1 (average)	*C*, M	h_2/h_1 (average)	*C*, M	h_2/h_1 (average)
2.8×10^{-7}	0.04 (2)	1.4×10^{-6}	0.04 (3)	1.3×10^{-9}	0.10 (2)	5×10^{-8}	0.06 (2)
2.5×10^{-6}	0.05 (3)	1.4×10^{-5}	0.10 (3)	1.3×10^{-8}	0.13 (2)	5×10^{-7}	0.12 (3)
1.4×10^{-5}	0.45 (3)	1.4×10^{-4}	0.13 (3)	1.3×10^{-7}	0.51 (3)	3×10^{-6}	0.54 (6)
1.6×10^{-4}	0.88 (2)			1.3×10^{-6}	0.64 (3)	2×10^{-5}	>1.0 (2)

[a] The number of experiments at a given *d*-metal concentration is indicated in parentheses.

An introduction of Ag^+ ions into system II to concentrations of 1×10^{-6}–1×10^{-4} M first results in a strong increase in the chemiluminescence intensity, the signal CL_a forming a broad flat maximum, and then the intensity smoothly decreases to 0 within ~20 min. At concentrations of Ag^+ ions exceeding 10^{-4} M an inhibition of chemiluminescence is first observed, then it blazes up rapidly to a flat maximum of signal CL_a, and at last it smoothly decreases as is the case with smaller silver additions.

As expected, the addition of Ni^{2+} or Co^{2+} ions to system II gave rise to a strong chemiluminescence flash at all studied concentrations of these ions. The peak height CL_a recorded on the addition of Ni^{2+} or Co^{2+} ions to system II was always greater by 50–70% than that for the same amount of a *d* metal added to system I. As the intensity of the initial chemiluminescence flash (signal CL_0) accompanying the dissolution of a ferrate sample in an alkaline luminol solution, as well as the intensity of the “permanent” luminescence (signal CL_s) of the resulting heterogeneous mixture, depended on the sample weight, we took the ratio of peak heights of signals CL_a (h_2) and CL_0 (h_1) as a characteristic of the analytical signal in system II.

The measured analytical signals (h_2/h_1) at various concentrations of one of four *d*-metal ions (Cd^{2+}, Ag^+, Ni^{2+}, or Co^{2+}) added to the system are shown in the table.

It is evident from the table that the ratio h_2/h_1 for these four ions “follows” the variation in the concentration of the ions, which increased in the experiments by 2–3 orders of magnitude. If the concentration of a *d* metal was varied within the limits of one order of magnitude, e.g., from 5×10^{-7} to 5×10^{-6} M in the experiment with Ni^{2+}, a linear dependence of h_2/h_1 on the concentration was observed (Fig. 3). It should be noted that for Cd^{2+}, Ni^{2+}, and Co^{2+} the both measured signals CL_0 and CL_a are sufficiently narrow, whereas in the case of Ag^+ the analytical signal is relatively broad, as noted before, and its height in the maximum may be only approximately compared to the height of the reference signal. When measuring the dependence of the chemiluminescence efficiency

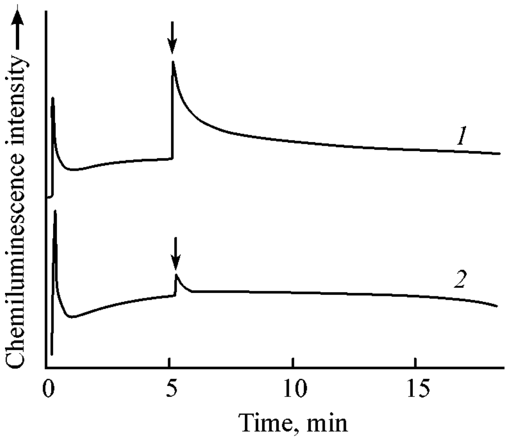


Fig. 2. Time dependence of chemiluminescence intensity at various concentrations of cadmium ions added to luminescent system II. Arrows denote the moments of Cd^{2+} addition. The first peaks in both curves are reference signals (h_1) and the second peaks, analytical signals (h_2). Concentration of Cd^{2+}, M: (*1*) 1.4×10^{-7} and (*2*) 1.6×10^{-4}.

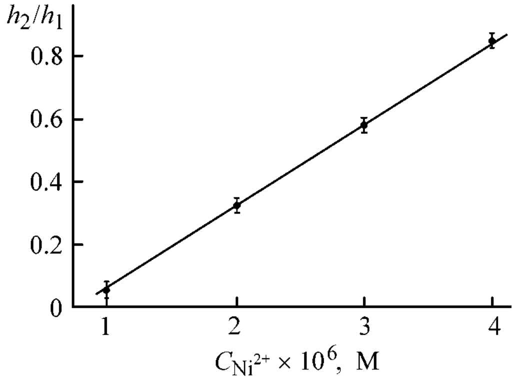


Fig. 3. Ratio h_2/h_1 as a function of the concentration of nickel ions.

on the Me^{n+} concentration in such cases, it is appropriate to measure the ratio of the areas of the signals CL_a and CL_0.

As the surface of Fe(III) hydroxide seems to participate in the chemiluminescence reaction in system II and the added *d* metal subsequently interacts with this surface, an addition of a surfactant can reveal the extent of this participation.

When studying the effect of a surfactant on the intensity of the analytical signal CL_a, we added to the standard alkaline solution of luminol a certain amount of one of surfactants: Sythofloc EM 8329 (anionic flocculant), Sythofloc EM 6159 (cationic flocculant), Sul'fonol, sodium lauryl sulfate, and the neutral surfactant Triton X-100. Then 9 ml of a solution containing a surfactant was introduced in a cell with a ferrate weighed sample, placed in a chamber of the measuring setup, and ~5 min after reaching a plateau of the chemiluminescence intensity 1 ml of $NiSO_4$ solution was introduced in the cell, and the time dependence of the chemiluminescence was measured. In all the experiments with surfactants the concentration of Ni^{2+} in the final solution (3×10^{-6} M) was constant and the concentration of the added surfactant depended on its type. Both flocculants had the concentration of 1.5 wt %; the final concentration of sodium lauryl sulfate in separate experiments was 1.5×10^{-4}, 1.5×10^{-3}, or 1.5×10^{-2} wt %; in experiments with Sul'fonol and Triton X-100 their concentrations of 1.5×10^{-3} wt % were constant. Seemingly small additions of surfactants should be compared with the amount of sodium ferrate(VI) in the system (~0.01–0.02 wt %).

The cationic flocculant showed the strongest effect: In its presence the measured "signal," i.e., the h_2/h_1 ratio, decreased by a factor of nine when Ni^{2+} was introduced in system II as compared to the same addition to system II free from the surfactant. The effect of Triton X-100 appeared to be very strong: The signal in its presence was weaker by a factor of ~3 than in its absence. In the other cases the relative intensity of chemiluminescence was insignificantly reduced (by 20–50%). The strong effect of the cationic flocculant is due to the fact that the surface of Fe(III) hydroxide is charged negatively.

Thus, the chemiluminescent oxidation of luminol has specific features compared to the reaction caused by hydrogen peroxide in the presence of *d*-metal ions.

EXPERIMENTAL

In this work we used "white" luminol and sodium ferrate(VI) Na_4FeO_5 prepared by the procedures in [12] and [13], respectively. Solutions of H_2O_2, KOH, and *d*-metal salts $AgNO_3$, $CdSO_4$, $NiSO_4$, and $CoSO_4$ were prepared from chemicals of chemically pure and ultrapure grades and from double-distilled water. Commercial flocculants Sythofloc EM 8329 (anionic) and Sythofloc EM 6159 (cationic) and also surfactants (Sul'fonol, sodium lauryl sulfate, and Triton X-100) were used without additional purification.

The chemiluminescence spectra and their variation in time were measured with a KSVU-1 universal spectral-computing complex [Leningrad Optical and Mechanical Association (LOMO), St. Petersburg] equipped with an MDR-2 monochromator and an FEU-100 photoelectron multiplier. The chemiluminescence in luminol oxidation with ferrate(VI) ions is observed as a broad structureless band in the range 350–530 nm with a maximum at 428 nm.

A weighed portion of sodium ferrate(VI) was introduced in a quartz cell with plane-parallel walls of volume 12 cm^3, the cell was placed in the chamber protected from light, and a standard alkaline solution of luminol was added with stirring. This solution of luminol in KOH had pH 12.3 and concentration of 2.5×10^{-4} M. A flash of chemiluminescence, lasting for a few seconds, was observed almost instantaneously; then the chemiluminescence intensity flattened out. On the whole the luminescence lasted for several tens minutes.

In the experiments on the effect of surfactant a required amount of a solution of a surfactant was added to the standard alkaline solution of luminol, then this solution was introduced in the measuring cell, and the further experiment was carried out as described above.

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