5. B. D. Lavrukhin, T. V. Strelkova, N. A. Chernyavskaya, and A. A. Zhdanov, *Vysokomol. Soedin.*, *A*, 1987, **29**, 272 [*Polym. Sci. USSR*, *A*, 1987, **29** (Engl. Transl.)].
6. B. D. Lavrukhin, N. A. Chernyavskaya, T. V. Strelkova, and A. A. Zhdanov, *Vysokomol. Soedin.*, *B*, 1988, **30**, 838 [*Polym. Sci. USSR*, *B*, 1988, **30** (Engl. Transl.)].
7. N. K. Gladkova, T. V. Strelkova, and B. G. Zavin, *Vysokomol. Soedin.*, *A*, 1995, **37** 496 [*Polym. Sci.*, *A*, 1995, **37** (Engl. Transl.)].
8. I. S. Akhrem, N. M. Chistovalova, S. M. Airapetyan, E. I. Mysov, and M. V. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1126 [*Bull. Acad. Sci. USSR, Div.Chem. Sci.*, 1978, **27**, 976 (Engl. Transl.)].
9. I. S. Akhrem, N. M. Chistovalova, D. V. Avetisyan, V. F. Sizoi, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1868 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36** (Engl. Transl.)].

Received March 25, 1996

Chemiluminescence in the oxidation of Na_2S by oxygen in water solutions

R. G. Bulgakov and L. A. Safonova*

Institute of Petrochemistry and Catalysis, the Bashkortostan Republic Academy of Sciences,
141 Prosp. Oktyabrya, 450075 Ufa, Russian Federation
Fax: 007 (3 472) 31 2750

Chemiluminescence was observed in the the oxidation of Na_2S by oxygen in aqueous solution. One of the luminescence emitters was identified as the triplet state $(SO_2)^*$ (λ_{max} = 420 nm) generated without participation of free radicals at the first stage of oxidation of Na_2S to $Na_2S_2O_3$. Oxygen is a necessary reagent for CL and isa quenching agent. CL was shown to increase in the presence of $Ru(bpy)_3Cl_2$ as a result of the transfer of energy from $(SO_2)^*$ to form $Ru(bpy)_3^{2+*}$, which emits at λ_{max} = 593 nm.

Key words: chemiluminescence, catalysis.

Weak chemiluminescence (CL) has been observed previously in the oxidation of aqueous solutions of $NaHSO_3$ (in the presence of metal salts)[1] and Na_2SO_3[2] by oxygen. The associate $(O_2)_2^*$ is the emitter in the former reaction (λ_{max} = 480 nm); in the second case the emitter is not identified. CL reactions of O_3 with sulfur-containing organic compounds and O atoms with CH_3SH, CH_3SCH_3, SO are also known,[3] where the triplet state of the $(SO_2)^*$ (λ_{max} = 340 nm) is the emitter.

Chemiluminescence was observed in the oxidation of Na_2S (**1**) by oxygen in aqueous solutions. A freshly prepared solution of **1** in water (10^{-2} mol L^{-1}, V = 20 mL) emits light ($I_{max} = 1.7 \cdot 10^5$ photon/s · mL), the intensity of which decreases 50 % after 3 min. This auto-CL disappears when O_2 is removed by evacuation or by bubbling the solution with N_2. After the introduction of O_2 into the solution of **1** the intensity of chemiluminescence jumps up and then begins to slowly decrease. A more pronounced jump in CL intensity is observed if N_2 has been preliminarily bubbled through the solution (Fig. 1). Thus, O_2 in this system is both the initiator of CL and the "quencher" of the CL emitter.

Products of the oxidation of **1** by oxygen are SO_2, $Na_2S_2O_3$ and Na_2SO_4.[4] We established that CL arises at the first stage of the oxidation that results in $Na_2S_2O_3$ formation. Oxidation of $Na_2S_2O_3$ and Na_2SO_3 by oxygen under similar conditions is not accompanied by CL. In contrast to the CL that occurs during $NaHSO_3$ oxidation, which is attributed to the recombination of free radicals $2\ HO_2^{\cdot} \rightarrow H_2 + (O_2)_2^*$, and is inhibited by the addition of phenol,[1] we did not observe a decrease in CL intensity with the addition of phenol (up to 10^{-4} mol L^{-1}) to the oxidized solution of **1**. This allows us to assume that in Na_2S oxidation CL occurs generates without the participation of free radicals. The CL spectrum that was measured with the help of cut-off filters consists of three maxima (Fig. 2). The solutions of **1** before and after oxidation do not possess noticable photoluminescence PL (300 K). It can be assumed that one of the emitters of CL in Na_2S oxidation is the triplet state $(SO_2)^*$ (λ_{max} = 420±15 nm). The nature of the other maxima of the CL spectrum are not clear yet. According to the data,[5] oxidation of Na_2S can proceed both with and without the formation of elemental sulfur.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1864—1865, July, 1996.

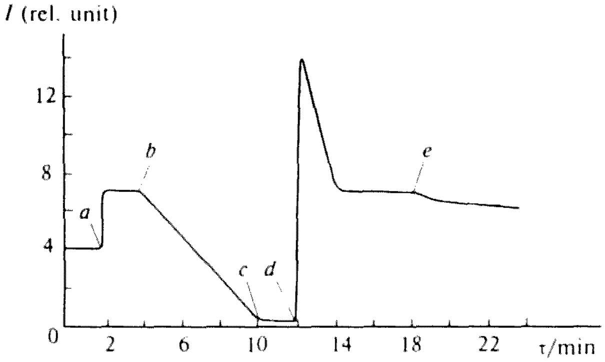

Fig. 1. Dependence of CL intensity (*I*) on time in the oxidation of Na_2S (10^{-2} mol L^{-1}, V = 20 mL, 300 K) by air oxygen in aqueous solutions. The following moments are marked by arrows: *a*, *d*; air bubble is on; *b*; air bubble is off and nitrogen bubble is on; *c*; nitrogen bubble is off (the part of the curve before moment *a* — auto-CL).

It was shown in direct experiments that when a sulfur suspension in water came in contact with O_2 no CL was observed. Therefore most probably formation of $(SO_2)^*$ occurs as a result of the oxidation of the primary intermediate SO (Scheme 1, reaction (1)).

Scheme 1

$$S^{2-} + O_2 \longrightarrow SO \xrightarrow{O_2} (SO_2)^* \longrightarrow$$

$$\longrightarrow SO_2 + h\nu_1\ (420\ \text{nm}) \qquad (1)$$

$$(SO_2)^* + [Ru(bpy)_3]^{2+} \longrightarrow SO_2 + [Ru(bpy)_3]^{2+*} \longrightarrow$$

$$\longrightarrow [Ru(bpy)_3]^{2+} + h\nu_2\ (593\ \text{nm})\ (2)$$

The proposed mechanism is analogous to the mechanism of CL in the oxidation of sulfur-containing compounds by ozone in the gaseous phase.[3] It does not include the step of S formation, in the contrast to the mechanism proposed for CL in the oxidation of sulfur-containing compounds by ozone in H_2SO_4 in the presence of CL emitters, lanthanide, or uranyl salts[6] (in the absence of these salts CL is caused by emission of the triplet state $(SO_2)^*$). The spectrum of nonactivated CL is not given[6] (only λ_{max} = 420 nm is mentioned).

Additions of aqueous solutions of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (**2**) activate CL (intensity increases 1.5 times when [Ru] = $5 \cdot 10^{-4}$ mol L^{-1}) as a result of the transfer of energy from $(SO_2)^*$ with the formation of $[Ru(bpy)_3]^{2+*}$, which emits light λ_{max} = 593±15 nm (Fig. 2; Scheme 1, reaction (2)).

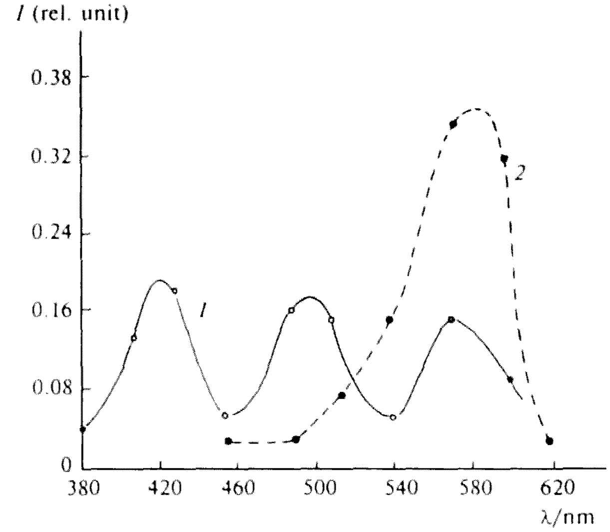

Рис. 2. CL spectra measured with the help of the set of cut-off filters in the oxidation of Na_2S (10^{-1} mol L^{-1}) by air oxygen in aquaous solutions without (*1*) and with addition of $Ru(bpy)_3Cl_2$ ($5 \cdot 10^{-4}$ mol L^{-1}) (*2*).

Experimental

Na_2S "pure for analysis" grade was purified by double recrystallization from oxygen-free bidistilled water, dried at 110 °C, and kept in a nitrogen atmosphere. The $Ru(bpy)_3Cl_2 \cdot 6H_2O$ complex was synthesized according to methods in Ref.7. Salts $Na_2S_2O_3$, Na_2SO_4, Na_2SO_3 of "chemically pure" and phenol of "pure for analysis" grades were used.

Absorption spectra were measured on a "Specord M-40" spectrophotometer. Photoluminescence spectra were recorded on a home-made specrtrofluorimeter, based on an MDR-29 scanning monochromator. The procedures of CL time-course and spectra measurement have been described earlier.[8]

References

1. J. Stauff, H. Schmidkunz, and G. Hartmann, *Nature*, 1963, **198**, 281.
2. B. V. Nekrasov, *Kurs obshchey khimii [Handbook of General Chemistry]*, Goskhimizdat, Moscow, 1962, 300 (in Russian).
3. H. Akimoto, B. J. Finlayson, and J. N. Pitts, *Chem. Phys. Lett.*, 1971, **12**, 199.
4. G. Charlot, *Bull. Soc. Chim.*, 1939, **6**, 1447.
5. G. S. Frenz, *Okislenie sulfidov metallov [Oxidation of Metal Sulfides]*, Nauka, Moskva, 1964, 58 p. (in Russian).
6. V. P. Kazakov, G. S. Parshin, R. G. Bulgakov, L. A. Khamidullina, D. D. Afonichev, *Radiokhimiya*, 1979, **21**, 199.
7. T. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.
8. R. G. Bulgakov. *Thesis Doctor of Science in Chemistry*, Institute of Organic Chemistry of the Ural Branch of the Academy of Sciences of USSR, Bashkir Science Center, Ufa, 1990, 446 p.

Received March 13, 1996