Brief Communications

Chemiluminescence in the interaction of organoboron peroxides with water

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Chemiluminescence (CL) was detected in the reactions of organoboron peroxides, intermediate products of the oxidation of 9-borabicyclo[3.3.1]nonane (**1**) by water. Triplet cyclooctanone emitting at λ = 420±15 nm is the emitter of CL. A mechanism for the formation of the excited ketone was suggested. The interaction of water with other components of the reaction mixture (the initial boron hydride **1**, end products of its oxidation, and a number of intermediate radicals) are not accompanied by CL.

Key words: chemiluminescence; organoboron compounds, hydrolysis, oxidation.

Previously,[1] chemiluminescence (CL) in the oxidation of solutions of organoboron hydrides in THF by O_2 caused by emission of the triplet cyclooctanone (hereinafter CL_1) has been reported. We found that the introduction of water into a solution of 9-borabicyclo[3.3.1]nonane (**1**) oxidized by dioxygen gives rise to a new CL (hereinafter CL_2) (Fig. 1, curves *2* and *3*).

Experimental

Compound **1** was synthesized by the interaction of cyclooctadiene with diborane;[2] cyclooctanone was obtained following the known procedure.[3] Cyclooctylhydroperoxide was synthesized by oxidation of cyclooctane by atmospheric oxygen in toluene in the presence of an initiator (α,α-azobisisobutyronitrile); THF was purified by distillation over sodium benzophenone ketyl. Bidistilled water was used in the experiments. The analysis of the products of oxidation of boron hydride **1** by O_2 and measurements of the CL, fluorescence (FL), and phosphorescence (PS) spectra have been described previously.[1] The content of organoboron peroxide in the course of autooxidation of compound **1** was determined by iodometric titration of the samples taken from the reaction solution.

Results and Discussion

In the case of autooxidation of compound **1** the reaction solution contains a complex mixture of substances: the initial boron hydride, stable products (alkoxides, ketones, organic peroxides, and hydrocarbons), and intermediates (organoboron peroxides (OBP) and $R^{\cdot}$, $RO^{\cdot}$, and $RO_2^{\cdot}$ radical species, where R is alkyl).[1,4–6] Certain of these products as well as the routes of their formation in the "dry" oxidation of compound **1** (without water additives) are shown in Scheme 1 (reactions (1) and (2)). All the components mentioned above can be potential participants of the reactions responsible for CL_2. However, addition of water (under an Ar atmosphere) to the initial (see Fig. 1, curve *1*) and to the completely oxidized boron hydride **1** (the solution of which no longer absorbs O_2) accompanied by violent evolution of H_2 as a result of reactions (1a) and (2a) does not lead to CL.

Thus, CL_2 is due to the reactions of the intermediate products of autooxidation of boron hydride **1**, *i.e.*, the necessary condition of its generation is the oxygen insertion into the B—C bond.

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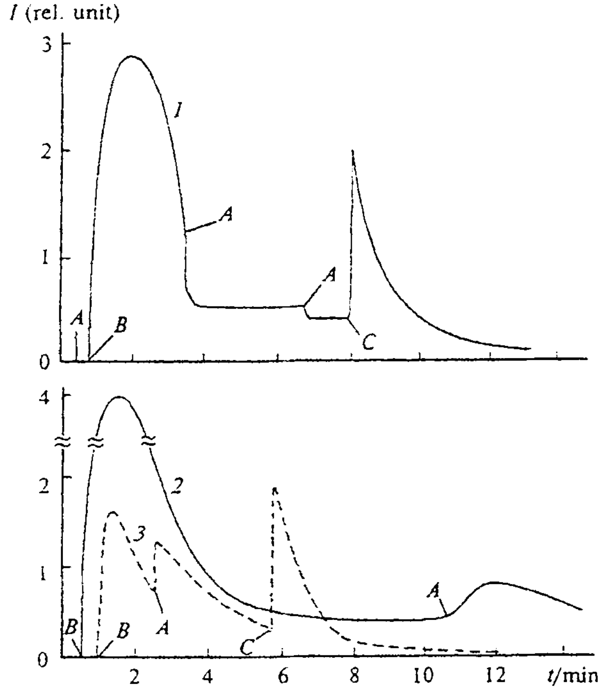


Fig. 1. Effect of water on CL kinetics in the oxidation of a solution of 9-borabicyclo[3.3.1]nonane (**1**) in THF (10 mL, T = 300 K): $[\mathbf{1}]$/mol L^{-1} = $1.1 \cdot 10^{-2}$ (*1*, *2*), $5 \cdot 10^{-3}$ (*3*); $[H_2O]$/mol L^{-1} = $2.7 \cdot 10^{-1}$ (*1*, *2*), $1.1 \cdot 10^{-1}$ (*3*) (calculation); *1*, H_2O was added to the initial boron hydride **1** prior to the moment air bubbling was switched on; *2*, H_2O was added in the course of oxidation; the moments of introducing water (*A*), switching on (*B*), and switching off (*C*) air bubbling are marked by arrows.

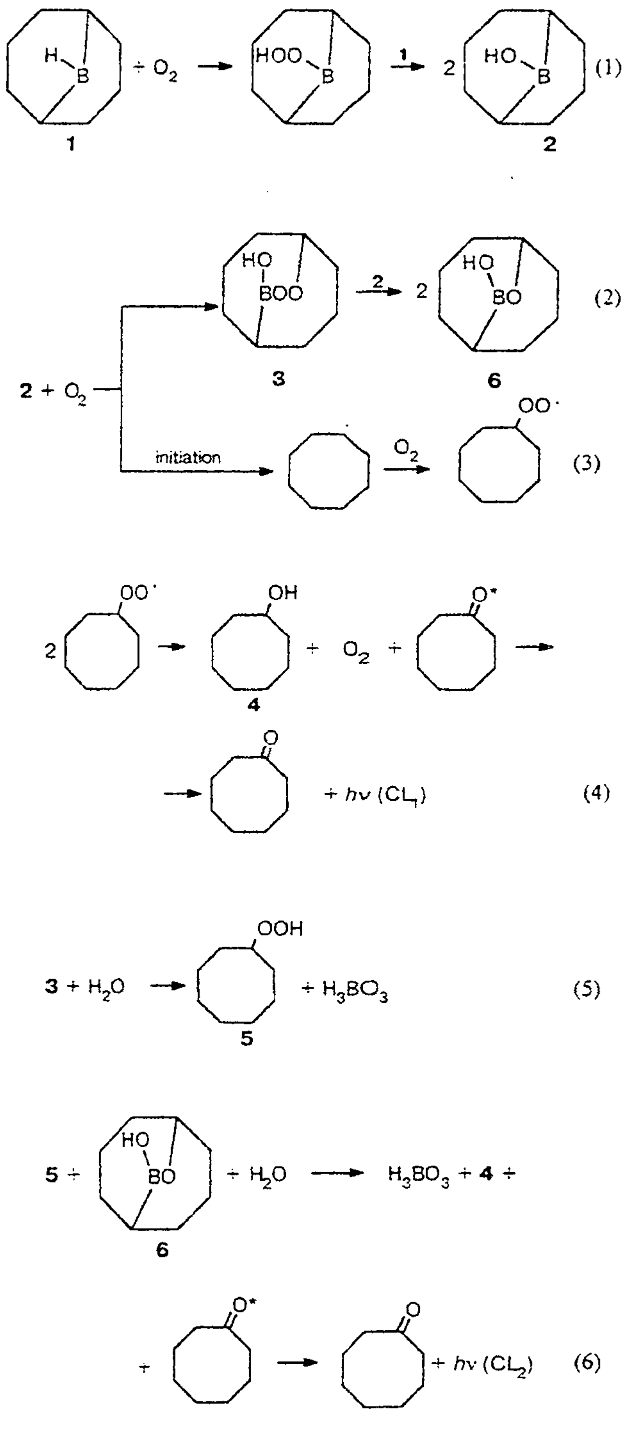
To elucidate the possibility of the appearance of CL in the interaction of water with the above-mentioned radicals formed in the oxidation of boron hydride **1**, water was added to the cyclooctane solution in the course of its oxidation by O_2. According to the published data on CL,[5,6] all types of radicals in question should be generated in the oxidation of cyclohexane in such a reaction solution.

No increase in CL appeared to occur in the presence of water (note that no CL during the oxidation of cyclooctane has been observed previously[7,8]). Hence, the reactions of $R^{\cdot}$, $RO^{\cdot}$, $RO_2^{\cdot}$ radicals with water cannot cause CL_2.

The totality of the results obtained allows one to conclude that CL_2 is due to the interaction of water with an OBP intermediate. This conclusion is confirmed by the fact that the intensity of CL_2 is proportional to the content of organoboron peroxides in the reaction solution (Fig. 2).

The CL_2 spectrum measured on the decay branch of the dependence of brightness on time lies in the region of emission of the triplet cyclooctanone and coincides with the PS spectrum of this ketone (Fig. 3). Thus,

Scheme 1



$$>BH + H_2O \longrightarrow >BOH + H^{\cdot} \qquad (1a)$$

$$H^{\cdot} + H^{\cdot} \longrightarrow H_2 + 104 \text{ kcal mol}^{-1} \qquad (2a)$$

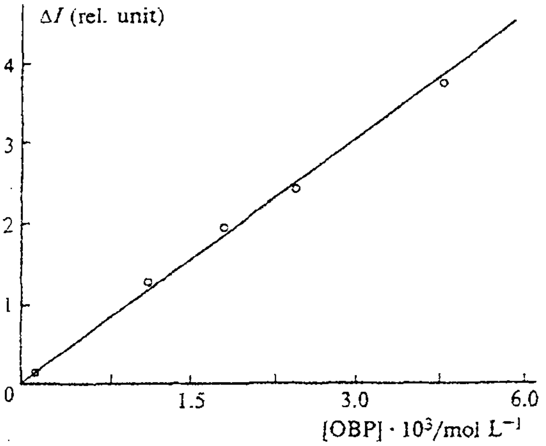


Fig. 2. Dependence of the intensity of the CL_2 burst (Δ*I*) on the OBP concentration determined iodometrically before adding water to the reaction solution of compound **1** in THF.

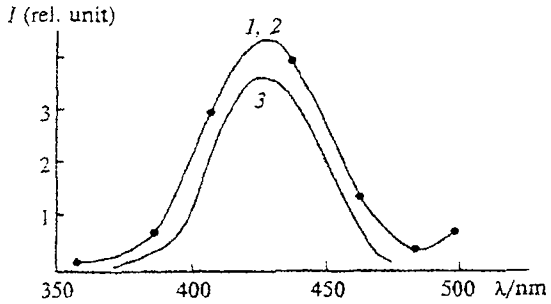


Fig. 3. The CL_2 spectrum (*1*) observed upon addition of water to the solution of compound **1** ($1.5 \cdot 10^{-3}$ mol L^{-1}) in THF in the course of its oxidation by air (6 min); $[H_2O]_0 = 1.1$ mol L^{-1} (calculation); water was added at the 6th min. The CL spectrum of the ROOH + oxidate mixture (the solution after the complete oxidation of **1**) (*2*). The PS spectrum of cyclooctanone (*3*) ($\lambda_{exc} = 320$ nm, $T = 77$ K).

triplet cyclooctanone is the emitter of both CL_1 and CL_2; however, the elementary stages of their generation are different.

The experimental results and the published data[9,10] suggest the following scheme of excitation of the CL_2 emitter (see Scheme 1). Usually, the mechanism of the "dark" autooxidation of metal alkyls includes both molecular and radical processes.[4] The mechanism of "dry" autooxidation with the formation of the products in the ground energy state is represented by reactions (1) and (2). Reactions (3) and (4) describe, in a simplified form, generation of the triplet cyclooctanone in the radical processes followed by CL_1. Organoboron peroxide **3** reacts with water to form hydroperoxide **5**, which further attacks the B—OR bond of the boron alkoxy derivative **6** to give the excited cyclooctanone emitting CL_2. The ability of organometallic peroxides to hydrolyze into hydroperoxides[9,10] as well as the presence of ketones (in the ground energy state) among the products of reactions of organic hydroperoxides with alkoxy derivatives of aluminium and boron alkyls[9] is in agreement with the suggested mechanism. Additionally, as was shown by special-purpose experiments, the addition of cyclooctylhydroperoxide ROOH to the solution of compound **1** completely oxidized by dioxygen (and hence containing boron alkoxy derivatives as main products) causes CL, whose spectrum coincides with that of CL_2.

Adding water in large excess to a solution of compound **1** under an Ar atmosphere followed by passing an air stream causes a rather bright CL (see Fig. 1, curve *1*), *i.e.*, even excess water does not result in the complete decomposition of boron hydride **1** (see reactions (1) and (2)). A further addition of water to the same solution not only fails to increase CL, but even quenches it (see Fig. 1, curve *1*). This effect of water on CL is due to the accumulation of OBP in the reaction solution prior to the moment when the first portion of H_2O was added. The amount of OBP is sufficient for the reaction with water to proceed at a rate when CL_2 dominates over CL_1. Large excess of water destroys OBP; as a result, the CL_2 contribution becomes too small to be detected against the CL_1 background.

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