## Letters to the Editor

## Chemiluminescence upon decomposition of dimethyldioxirane in the presence of aromatic hydrocarbons

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Previously, an ester in an electronically excited state was expected to be formed only upon the thermal isomerization of dioxiranes.<sup>1</sup> However, chemiluminescence (CL) was not observed during the thermolysis, which might be due to a low efficiency of the fluorescence and phosphorescence of the esters. In the present work CL upon the thermal decomposition of dimethyldioxirane (1) in the presence of CL activators, aromatic hydrocarbons, was evidenced for the first time.

Dimethyldioxirane was synthesized as described in Ref. 2. The analysis of dimethyldioxirane was carried out according to the procedure reported in Ref. 3. 9,10-Diphenylanthracene (DPA), dibromoanthracene (DBA), and anthracene (A) were used as activators (Act). DPA and A are activators of the singlet states, while DBA is an activator of the triplet electronically excited states. The total volume of the reaction mixture was 3 ml with the starting concentrations of the reagents:  $[1] = 2 \cdot 10^{-2} \text{ mol/L}$  and  $[Act] = 6.7 \cdot 10^{-4} \text{ mol/L}$ (solvent – acetone, temperature 35 °C). The CL spectral region (estimated by means of light filters), which corresponded to the fluorescence spectra of activators (380-450 nm for A, and 380-480 nm for DBA and DPA), showed that the above-mentioned aromatic hydrocarbons were the radiation emitters.

The activators increase the consumption rate  $(W/mol \cdot (L \cdot s)^{-1})$  of compound 1, measured by the CL

technique, in the following sequence:  $1.2 \cdot 10^{-4}$  (DBA);  $6.8 \cdot 10^{-4}$  (A);  $38.0 \cdot 10^{-4}$  (DPA). The glow of the activators was more intense for DBA. The absorption spectra of solutions taken before and after the reaction completion showed that DPA and A were oxidized, while DBA was inert toward 1 (Fig. 1). DBA does not react because of its higher oxidation potential compared with that of DPA and A. At the same time DBA induces decomposition of 1 and activates the triplet-excited methyl acetate (2) formed in the reaction:

$$\begin{array}{c} H_{3}C \\ H_{3}C \\ H_{3}C \\ \end{array} \xrightarrow{O} + DBA \longrightarrow \begin{bmatrix} {}^{3}O^{\star} \\ CH_{3} - \overset{U}{C} - OCH_{3} \cdots DBA \end{bmatrix} \longrightarrow \\ 1 \\ \hline \\ CH_{3} - \overset{U}{C} - OCH_{3} + DBA^{\star} \\ 2 \\ \hline \\ DBA + hv \end{array}$$

A comparison of the intensities of the activated CL and the rates of the glow damping allows one to assume that excitation of DPA and A in the reaction with 1 takes another route and is likely to proceed according to the reversible electron transfer mechanism (the mechanism was used previously to explain the chemi-



Fig. 1. Absorption spectra of DPA (a), A (b), and DBA (c) solutions before (1) and after (2) reaction completion.



luminescence of a dioxirane intermediate postulated in the reaction of geminal dichloroderivatives of hydrocarbons with sodium peroxide<sup>4</sup>).

## References

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