Russian Chemical Bulletin, International Edition, Vol. 56, No. 2, pp. 205—210, February, 2007

Chemiluminescence during decomposition of 1,4-dimethylnaphthalene endoperoxide on the silica gel and alumina surface

D. V. Kazakov,[a]★ D. V. Mal´tsev,[a] G. Ya. Maistrenko,[a] S. L. Khursan,[b] M. Yu. Ovchinnikov,[b] and V. P. Kazakov[a]

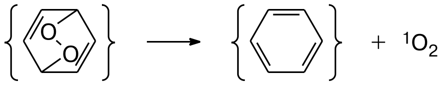
[a]Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066. E-mail: chemlum@anrb.ru; dmitri_kazakov@mail.ru
[b]Department of Chemistry, Bashkir State University,
32 ul. Frunze, 450007 Ufa, Russian Federation.
Fax: +7 (347 2) 33 1677

Decomposition of 1,4-dimethylnaphthalene endoperoxide supported on the silica gel and alumina surface is accompanied by chemiluminescence (CL) in the IR and visible spectral regions. The CL emitter in the IR region is singlet oxygen. The $^1O_2$ dimol contributes mainly to the emission at λ_{max} = 630 and 700 nm. It was shown by the IR-CL method that endoperoxide decomposition on the sorbent surface follows the first-order kinetics. The activation parameters of the process were determined. On the Al_2O_3 and silica gel surfaces a substantial acceleration of the decomposition of 1,4-dimethylnaphthalene endoperoxide is observed compared to the solution.

Key words: chemiluminescence, singlet oxygen, endoperoxides, alumina, silica gel.

Singlet oxygen $^1O_2$ plays an important role in organic synthesis, biochemistry, and medicine and evokes constant interest for investigation of chemi- and bioluminescence.[1—8] Reactions of hydrogen peroxide with ClO^- and metals (*e.g.*, MoO_4^{2-}) and decomposition of peroxy complexes and trioxides are most frequently used for the chemical generation of singlet oxygen.[1] Along with these processes, the thermal decomposition of endoperoxides accompanied by a high yield of excited oxygen generation is widely used.[7,8] Endoperoxides are rather inert, which makes it possible to avoid side oxidation reactions when they are used as sources of singlet oxygen in organic synthesis. In addition, endoperoxides are relatively stable at room temperature compared, *i.e.*, with trioxides,[9] and a rather wide set of the presently synthesized derivatives allows one to study the properties of this class of compounds in both organic and aqueous media.[7,8] Remarkably, in the case of endoperoxides, the formation of the singlet state ($^1O_2$) is a result of the simple monomolecular reaction of peroxide decomposition to the initial hydrocarbon and oxygen (Scheme 1), which makes these compounds to be a good model for studying the elementary act of chemiexcitation.

Scheme 1



Many works (see reviews[7,8]) are devoted to the study of various aspects of chemical transformations of endoperoxides in solutions (yields of $^1O_2$, products, mechanism, and kinetics of decomposition). Data concerning the behavior of endoperoxides on the solid surface are lacking. At the same time, it is known that the decomposition of peroxy compounds can considerably be accelerated on the surface, which, in addition, sometimes affects the processes affording products in the electron-excited state.[10] In addition, data on stability of endoperoxides can be helpful when using these compounds as sources of singlet oxygen for oxidation on a solid support.

Therefore, in the present work 1,4-dimethylnaphthalene endoperoxide (MNEP) was used as an example to study the behavior of endoperoxides sorbed on the alumina and silica gel surface.

Experimental

Synthesis of MNEP was carried out according to a described procedure[11,12] but with insignificant modifications.

A glass reactor cooled to 0 °C was loaded with CH_2Cl_2 (18 mL), freshly distilled 1,4-dimethylnaphthalene (1 mL, ~1 g), and methylene blue (2 mg) dissolved in CH_2Cl_2 (1 mL). The reaction was carried out with continuous oxygen purging and irradiation with a DKSSh xenon lamp (1000 W) through the light filter with the transmission wavelength >500 nm to prevent the photodestruction of MNEP that formed. After ~30 h the synthesis was stopped, and the solution was passed through a column with neutral alumina (l = 10 cm, d = 3.5 cm) to

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 199—204, February, 2007.

1066-5285/07/5602-0205 © 2007 Springer Science+Business Media, Inc.

remove methylene blue (water-jet pump was used for faster passing the solution through Al_2O_3). Some portion of the endoperoxide was sorbed on the column and washed with a new portion of CH_2Cl_2. Then CH_2Cl_2 was removed *in vacuo*, and the mixture of unreacted 1,4-dimethylnaphthalene and its endoperoxide was repeatedly recrystallized from a heptane—CH_2Cl_2 (10 : 1) mixture at 0 °C. As a result, a white crystalline powder of the endoperoxide (~200 mg) was obtained and stored in the dark at –20 °C.

1,4-Dimethylnaphthalene endoperoxide was identified using ^1H NMR on a Bruker AM 300 spectrometer (300 MHz) by the characteristic signal[11] of protons of the methyl group in the endoperoxide at δ 1.85 in $CDCl_3$ (signals of other protons, δ: 6.70 (s, 2 H); 7.21, 7.29 (both dd, 1 H each, J = 7.4 Hz, J = 7.5 Hz); 7.33, 7.40 (both d, 1 H each, J = 7.5 Hz)).

Quantitative analysis of the endoperoxide was carried out by ^1H NMR in $CDCl_3$ using acetone as the standard. Purity of the product was 100%.

The sorbent surface was modified by MNEP as follows. A solution (0.5 mL) of the endoperoxide in CCl_4 was added to silica gel or Al_2O_3 (0.1 g) at 0 °C. The suspension was stirred, and the solvent was removed *in vacuo*.

Carbon tetrachloride was purified and dried using a known procedure.[13] 1,4-Dimethylnaphthalene was purified by vacuum distillation. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was repeatedly recrystallized from bidistilled water.

Silica gel with a surface area of 600 $m^2\ g^{-1}$ and a particle size of 0.125—0.160 mm, 0.160—0.200 mm, or 7.5 μm and acidic, neutral, and basic silica were used. Silica gel and Al_2O_3 were calcined prior to use for 3 h at 150 °C. In all entries, a weighed sample of alumina and silica gel was 100 mg.

Chemiluminescence (CL) in the IR spectral region was detected on a setup described earlier[10] using a FEU-83 photomultiplier tube sensitive in the IR range and cooled to –60 °C. The range of singlet oxygen emission was picked out using the IKS-7 boundary light filter (λ = 1000—1300 nm). Chemiluminescence in the visible spectral range arising during MNEP decomposition was detected on a setup equipped with a FEU-119 photomultiplier tube sensitive in the visible spectral range (λ from 330 to 750 nm). The CL spectrum was obtained using boundary light filters placed in a holder between the bottom of the temperature-controlled cell containing a sample and the photocathode of the FEU tube under the following conditions: 60 °C, [MNEP] = $1 \cdot 10^{-4}$ mol g^{-1} (on silica gel) and [MNEP] = $2 \cdot 10^{-4}$ mol g^{-1} (on Al_2O_3). In particular entries, CL was detected through the interference light filter (λ = 700 nm) at 70 (on silica gel) and 80 °C (on Al_2O_3).

Quantum chemical calculations were performed using the Gaussian 98, Revision A.7 program.[14] The structures of MNEP and its decomposition products were determined by the complete optimization of geometric parameters of molecules. When the thermal effect of MNEP decomposition was calculated, the electron correlation energy was taken into account in the framework of the density functional theory (DFT). The Becke three-parameter hybrid functional[15] was used in combination with the Lee—Yang—Parr correlation functional.[16] The triple-valence-split basis set including sets of polarization functions of the d- and p-types was used to construct molecular orbitals; thus, the B3LYP/6-311G(d,p) approximation was used. The $\Delta H°$ value was determined using the total energies of participants of the reaction.

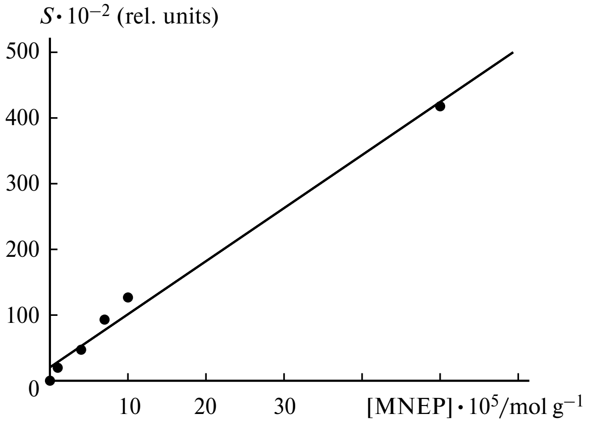
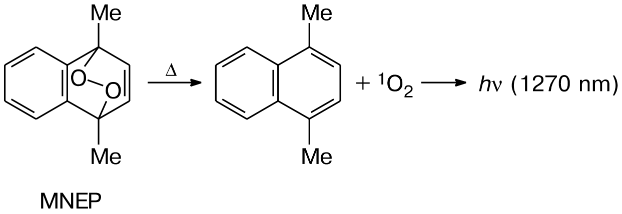


Fig. 1. Plot of the total IR-CL intensity (S) arising upon the MNEP decomposition at 70 °C on neutral alumina *vs.* amount of the supported endoperoxide.

Results and Discussion

Chemiluminescence in the IR spectral range. Thermolysis of MNEP on the silica gel and alumina surface is accompanied by CL in the IR spectral range (λ > 1000 nm). As can be seen from the data in Fig. 1, the total IR-CL intensity (S) is proportional to the concentration of endoperoxide supported on the Al_2O_3 surface (similar data were obtained on silica gel). Evidently, as in solution,[1] singlet oxygen is the light emitter on the surface in the IR range (Scheme 2).

Scheme 2



An additional argument in favor of $^1O_2$ formation is a considerable weakening of the IR-CL intensity in the presence of DABCO, which is a known quencher[17] of $^1O_2$ luminescence when supporting on both the Al_2O_3 and silica gel surfaces. For instance, in the presence of DABCO supported on silica gel ([DABCO] = $2.7 \cdot 10^{-4}$ mol g^{-1}; silica gel 600 $m^2\ g^{-1}$, 0.125—0.160 mm), the total IR-CL intensity upon endoperoxide decomposition ($5 \cdot 10^{-5}$ mol g^{-1}) at 60 °C is by 2.7 times lower than that in the absence of DABCO. The quenching effect on alumina is more considerable: in the presence of even $1 \cdot 10^{-4}$ mol g^{-1} DABCO supported on acidic Al_2O_3, the IR-CL signal for the MNEP decomposition ($1 \cdot 10^{-4}$ mol g^{-1}) at 60 °C is not observed at all.

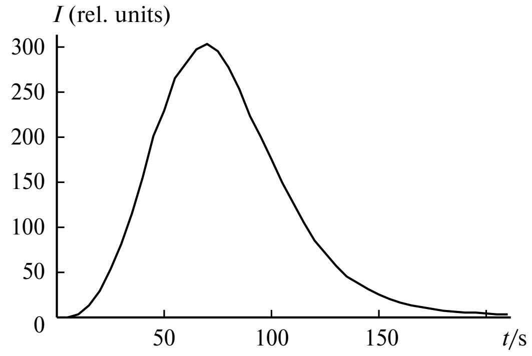


Fig. 2. Typical kinetic curve of singlet oxygen IR-CL decay on the silica gel surface upon the MNEP decomposition (90 °C; [MNEP] = $1 \cdot 10^{-4}$ mol g^{-1}; silica gel 0.160—0.200 mm, 600 m^2 g^{-1}).

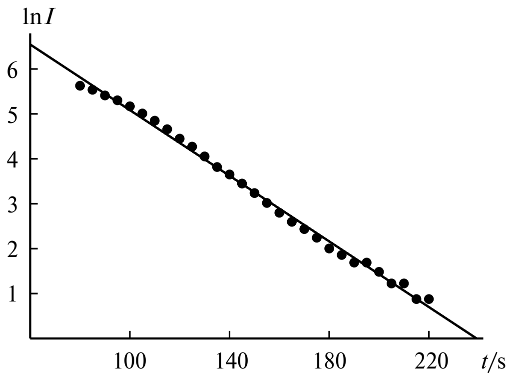


Fig. 3. Semilogarithmic anamorphosis of the kinetic curve of IR-CL decay upon the MNEP decomposition on the silica gel surface (90 °C; [MNEP] = $1 \cdot 10^{-4}$ mol g^{-1}; silica gel 0.160—0.200 mm, 600 m^2 g^{-1}).

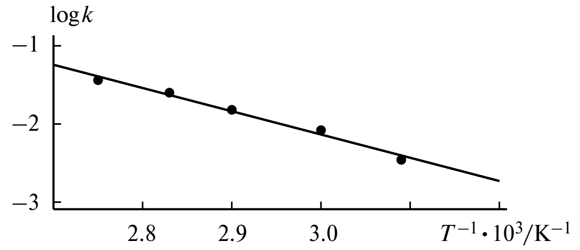


Fig. 4. Temperature plot of the rate constant of MNEP decomposition (k) on silica gel ([MNEP] = $1 \cdot 10^{-4}$ mol g^{-1}; silica gel 0.160—0.200 mm, 600 m^2 g^{-1}).

Table 1. Rate constants of the MNEP consumption (k) on silica gel (0.125—0.160 mm, 600 m^2 g^{-1}) and neutral alumina at 70 °C

Silica gel		Alumina	
$[\text{MNEP}] \cdot 10^5$ /mol g^{-1}	$k \cdot 10^3$ /s^{-1}	$[\text{MNEP}] \cdot 10^4$ /mol g^{-1}	$k \cdot 10^3$ /s^{-1}
1	13.1	1	10.1
4	12.6	4	10.5
7	14.9	7	7.6
10	13.3	10	12.1
50	13.8	50	11.5

The time dependence of the IR-CL intensity arising upon the MNEP decomposition on the silica gel surface is presented in Fig. 2. The kinetics of IR-CL decay upon the MNEP decomposition on the alumina surface is similar. As can be seen from the data presented in Fig. 2, the curve passes through the maximum caused by heating of the endoperoxide to the required temperature. The region of the curve after the maximum reflects the decomposition of the endoperoxide on the sorbent surface obeying the first-order law (Fig. 3). The rate constant found from the semilogarithmic anamorphoses of the kinetic curves of IR-CL decay is independent of the amount of the endoperoxide supported on Al_2O_3 and silica gel (Table 1).

The temperature dependence of the rate constant of MNEP decomposition on the silica gel and alumina surface was studied. The plot of log$k$ *vs.* $1/T$ obtained on silica gel is shown in Fig. 4. The activation energies (E_a) and pre-exponential factors (log$A$) for the endoperoxide decomposition were determined by the temperature plots. As can be seen from the data in Table 2, the activation parameters of the process are virtually independent of the properties of the silica gel surface, whereas they are lower than those on Al_2O_3, except for the parameters for basic alumina, where the E_a and log$A$ values are close to those obtained on silica gel. Comparison of the obtained results (see Table 2) with published data[12] on the MNEP decom-

Table 2. Activation parameters (E_a and log$A$) of the MNEP decomposition on the silica gel and alumina surfaces ([MNEP] = $1 \cdot 10^{-4}$ mol g^{-1})*

Silica gel**	E_a /kcal mol^{-1}	log$A$	Alumina	E_a /kcal mol^{-1}	log$A$
0.125—0.160 mm	14.5	7.3	Acidic	17.4	9.0
0.160—0.200 mm	13.6	6.8	Neutral	16.3	8.4
7.5 μm	12.6	6.1	Basic	13.0	6.3

* Measurements were carried out in the 50—90 °C interval.

** The particle size is indicated. In all cases, the surface area was 600 m^2 g^{-1}.

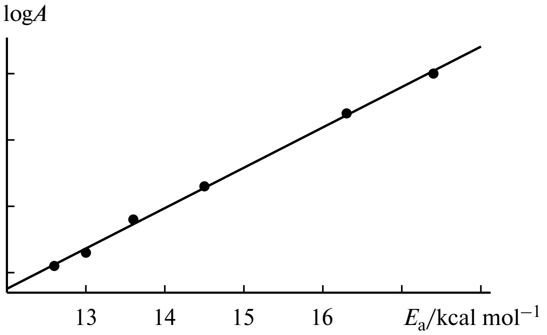


Fig. 5. Plot of log*A* *vs.* activation energy (E_a) of the MNEP decomposition on the silica gel and alumina surfaces ([MNEP] = $1 \cdot 10^{-4}$ mol g^{-1}). The E_a and log*A* values are given by the data in Table 2.

position in solution (E_a = 24.8 kcal mol^{-1}, log*A* = 13.7, solvent 1,4-dioxane) shows that the silica gel and Al_2O_3 surfaces substantially catalyze the decomposition of endoperoxide.

It should be mentioned that the activation parameters of endoperoxide decomposition obtained by the IR-CL method on different surfaces obey the compensation relationship log$A = 0.6E_a - 1.5$ (r = 0.99) (Fig. 5), which is characteristic of heterogeneous reactions and also of one-act processes of temperature quenching of luminescence of both organic compounds[18] and lanthanide ions.[19]

It is known[1,10,20] that the sum of the enthalpy ($\Delta H°$) and activation energy of the reaction should be higher or at least equal to the energy of the electron-excited state of the process for the excited state to be formed in the chemical reaction. Our DFT calculations showed that the MNEP decomposition is exothermic: $\Delta H°$ = -17 kcal mol^{-1}. Thus, the sum of the activation energy of endoperoxide decomposition (13—17 kcal mol^{-1}, see Table 2) and $\Delta H°$ is more than enough for the transition of oxygen to the excited $^1\Delta_g$ state, which lies[2] at a level of 22.5 kcal mol^{-1}. It is of interest that, according to experimental data,[12] the decomposition of crystalline polyaromatic 1,4-endoperoxides is an endothermic reaction ($\Delta H°$ = +2—9 kcal mol^{-1}). In authors´ opinion,[12] triplet oxygen is excited exclusively due to the activation energy. We believe that the experimentally measured enthalpy of the reaction[12] is, in fact, the value including thermal effects related to the deformation and destruction of endoperoxide crystals along with the decomposition of the endoperoxide itself (which is exothermic in fact). If the MNEP decomposition is endothermic, at least no chemiluminescence of singlet oxygen would be observed on silica gel and alumina, because only the activation energy of the process (13—17 kcal mol^{-1}) is not enough for $^1O_2$ formation.

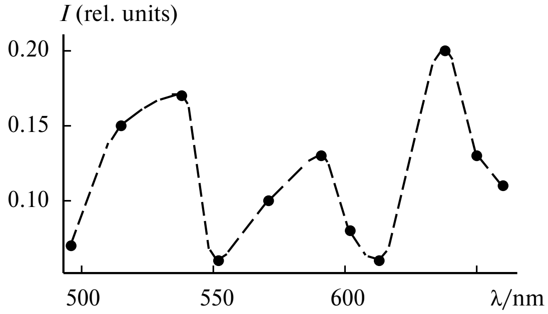


Fig. 6. Chemiluminescence spectrum appeared upon the MNEP decomposition on the acidic alumina surface at 60 °C ([MNEP] = $2 \cdot 10^{-4}$ mol g^{-1}).

Chemiluminescence in the visible spectral range. In addition to IR-CL, the decomposition of the endoperoxide on the silica gel and alumina surface is accompanied by the emission in the visible spectral range. The CL spectrum in the MNEP decomposition on both neutral and acidic alumina (Fig. 6) recorded using the boundary light filters is rather complicated with emission maxima at λ = 500—540, 560—600, and 600—650 nm. The CL spectrum appeared upon the endoperoxide decomposition on silica gel (0.125—0.160 mm, 600 m^2 g^{-1}) is similar with the only difference that it contains a weak emission band at λ = 450—500 nm. In addition, the decomposition of the endoperoxide on both Al_2O_3 and silica gel is accompanied by the emission through the interference filter at λ = 700 nm.

It can be assumed that the maxima at λ = 560—600 and 600—650 nm, as well as the luminescence at λ = 700 nm, are caused by radiative transitions[1,21] in a molecule of singlet oxygen dimol $(^1O_2)_2$

$$(^1\Delta_g)_{v=1}(^1\Delta_g)_{v=0} \rightarrow (^3\Sigma_g{}^-)_{v=0}(^3\Sigma_g{}^-)_{v=0}\ (\lambda_{max} = 578\ \text{nm}),$$

$$(^1\Delta_g)_{v=0}(^1\Delta_g)_{v=0} \rightarrow (^3\Sigma_g{}^-)_{v=0}(^3\Sigma_g{}^-)_{v=0}\ (\lambda_{max} = 633\ \text{nm}),$$

$$(^1\Delta_g)_{v=0}(^1\Delta_g)_{v=0} \rightarrow (^3\Sigma_g{}^-)_{v=1}(^3\Sigma_g{}^-)_{v=0}\ (\lambda_{max} = 703\ \text{nm}).$$

Note that the CL of singlet oxygen dimol upon the MNEP decomposition in solution has been reported earlier.[22—24] The formation of $(^1O_2)_2$ on the solid surface is also favored by the fact of luminescence weakening in the visible spectral range in the presence of the DABCO supported on the surface. For instance, the total CL intensity of MNEP decomposition ($1 \cdot 10^{-4}$ mol g^{-1}) at 60 °C on the surface of acidic Al_2O_3 at λ > 600 nm in the presence of $1 \cdot 10^{-4}$ and $2 \cdot 10^{-4}$ mol g^{-1} DABCO is lower by 3 and 5 times, respectively, than that in the absence of DABCO. Similar effect of quenching of the CL intensity is observed on silica gel: the ratio of the total CL intensities (λ > 620 nm) upon the endoperoxide decomposition ($5 \cdot 10^{-5}$ mol g^{-1}) at 60 °C on silica gel (0.125—0.160 mm, 600 m^2 g^{-1}) in the absence and presence of DABCO ($2.7 \cdot 10^{-4}$ mol g^{-1}) is 1.54.

An additional argument in favor of dimol formation is the effect of oxygen on the CL intensity at λ = 700 nm. It is known from literature data[25] on the photosensitized

$^1O_2$ generation that in solution triplet oxygen quenches the dimol luminescence at $\lambda = 700$ nm. According to our data on the endoperoxide decomposition (70 °C) on the silica gel surface (0.125—0.160 mm, 600 $m^2 g^{-1}$), the total chemiluminescence intensity at $\lambda = 700$ nm in an oxygen atmosphere is by 1.2 times lower than that in argon, whereas the ratio of the total IR-CL intensities of singlet oxygen is virtually the same in O_2 and argon.

Remarkably, for the MNEP decomposition on both silica gel and alumina the ratios of the total intensities of chemiluminescence arising in the IR spectral range and at $\lambda = 700$ nm (taking into account the spectral sensitivity of the FEU tube) differ insignificantly and range within 460—590. For instance, when $1 \cdot 10^{-4}$ mol g^{-1} endoperoxide decomposes on silica gel (0.125—0.160 mm, 600 $m^2 g^{-1}$) $S_{\text{IR-CL}}/S_{\lambda=700} = 570$ (70 °C), 590 (80 °C), and 530 (90 °C), and for the MNEP concentration equal to $5 \cdot 10^{-4}$ mol g^{-1} on silica gel (0.160—0.200 mm, 600 $m^2 g^{-1}$) $S_{\text{IR-CL}}/S_{\lambda=700}$ is 470 (70 °C). Similar $S_{\text{IR-CL}}/S_{\lambda=700}$ value (464) was obtained on acidic alumina ([MNEP] = $1 \cdot 10^{-4}$ mol g^{-1}, 80 °C). This fact additionally evidences that the light emitter at $\lambda = 700$ nm on silica gel and Al_2O_3 has the single nature. The considerably lower CL intensity in the visible spectral range compared to the IR-CL intensity is caused by the very low stationary concentration of $(^1O_2)_2$, which is due to the high constant of its dissociation (10^{10}—10^{11} s^{-1}).[25—28]

Nevertheless, singlet oxygen dimol is not, most likely, the only emitter in the visible spectral range. Indeed, the results presented above show that in the IR spectral region DABCO on silica gel quenches the emission of $^1O_2$, which is a dimol precursor, by 2.7 times, whereas in the visible spectral range at $\lambda > 620$ nm the CL is weakened by 1.5 times only. Although DABCO completely quenches the IR-CL of $^1O_2$ on Al_2O_3, the emission at $\lambda > 600$ nm, nevertheless, is quenched incompletely. Evidently, the luminescence spectrum at $\lambda > 600$ nm contains a component that is not related to $(^1O_2)_2$. It is most likely that the CL at $\lambda < 560$ nm is also caused not by singlet oxygen dimol. Perhaps, it is caused by the decomposition of an admixture of peroxides formed in the step of MNEP synthesis and is not separated upon recrystallization. The concentration of the admixture is probably very low, because it is not detected by ^1H NMR. At the same time, it cannot be ruled out that, unlike solution, the sorbent surface provides other routes of endoperoxide decomposition in addition to the reaction shown in Scheme 2. These routes are responsible for the chemiluminescence observed at $\lambda < 560$ nm.

Thus, it is shown in the present work that the decomposition of 1,4-dimethylnaphthalene endoperoxide supported on the silica gel or alumina surface is accompanied by chemiluminescence in the IR and visible spectral regions. Singlet oxygen is the light emitter in the IR range. It was found by the IR-CL method that the decomposition of the endoperoxide on the sorbent surface obeys the first-order law. The activation parameters of the process determined show that the surface substantially catalyzes the endoperoxide decomposition compared to the process in solution. In addition to IR-CL, the endoperoxide thermolysis is accompanied by chemiluminescence in the visible spectral region. It is assumed that singlet oxygen dimol $(^1O_2)_2$ contributes substantially to the CL at $\lambda_{\max} =$ 630 and 700 nm.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32663a), the Council on Grants of the President of the Russian Federation (Program of State Support for Leading Scientific Schools of the Russian Federation, Grant NSh-5486.2006.3), and the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Program of Fundamental Research "Theoretical and Experimental Investigation of the Chemical Bond Nature and Mechanisms of the Most Important Chemical Reactions and Processes").

References

1. W. Adam, D. V. Kazakov, and V. P. Kazakov, *Chem. Rev.*, 2005, **105**, 3371.
2. C. Schweitzer and R. Schmidt, *Chem. Rev.*, 2003, **103**, 1685.
3. E. L. Clennan, *Tetrahedron*, 2000, **56**, 9151.
4. K. Briviba and H. Sies, *Method. Enzymol.*, 2000, **319**, 222.
5. W. Adam and T. Wirth, *Acc. Chem. Res.*, 1999, **32**, 703.
6. A. A. Krasnovsky, Jr, *Biologich. Membrany*, 1998, **15**, 530 [*Membr. Cell Biol.*, 1998, **12**, 665 (Engl. Transl.)].
7. J. M. Aubry, C. Pierlot, J. Rigaudy, and R. Schmidt, *Acc. Chem. Res.*, 2003, **36**, 668.
8. C. Pierlot, J. M. Aubry, K. Briviba, H. Sies, and P. Di Mascio, *Method. Enzymol.*, 2000, **319**, 3.
9. V. V. Shereshovets, S. L. Khursan, V. D. Komissarov, and G. A. Tolstikov, *Usp. Khim.*, 2001, **70**, 123 [*Russ. Chem. Rev.*, 2001, **70**, 105 (Engl. Transl.)].
10. G. L. Sharipov, V. P. Kazakov, and G. A. Tolstikov, *Khimiya i khemilyuminestsentsiya 1,2-dioksetanov* [*Chemistry and Chemiluminescence of 1,2-Dioxetanes*], Nauka, Moscow, 1990, 288 pp. (in Russian).
11. H. H. Wasserman and D. L. Larsen, *J. Chem. Soc., Chem. Commun.*, 1972, **5**, 253.
12. N. J. Turro, M.-F. Chow, and J. Rigaudy, *J. Am. Chem. Soc.*, 1981, **103**, 7218.
13. A. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley, New York, 1972, 541 pp.
14. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. Millam, M. A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz,

B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98 (Revision A.7)*, Gaussian, Inc., Pittsburgh (PA), 1998.

15. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
16. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
17. F. Wilkinson, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1995, **24**, 663.
18. V. P. Kazakov, *Optika i Spektroskopiya*, 1965, **18**, 54 [*Optics Spectroscopy*, 1965, **18** (Engl. Transl.)].
19. V. P. Kazakov, *Teor. Eksp. Khim.*, 1968, **4**, 424 [*Theor. Exp. Chem.*, 1968, **4** (Engl. Transl.)].
20. W. Adam and R. Curci, *Chim. Ind. (Milan)*, 1981, **63**, 20.
21. A. U. Khan, *Int. J. Quant. Chem.*, 1991, **39**, 251.
22. W. Adam, V. P. Kazakov, D. V. Kazakov, R. R. Latypova, G. Ya. Maistrenko, D. V. Mal´zev, and F. E. Safarov, in *Bioluminescence and Chemiluminescence: Progress and Perspectives*, Eds A. Tsuji, M. Matsumoto, M. Maeda, L. J. Kricka, and P. E. Stanley, World Scientific, Singapore, 2005, 135.
23. Y. Fu, A. A. Krasnovsky, Jr, and C. S. Foote, *J. Am. Chem. Soc.*, 1993, **115**, 10282.
24. P. Di Mascio, E. J. H. Bechara, and J. C. Rubim, *Appl. Spectrosc.*, 1992, **46**, 236.
25. P.-T. Chou, Y.-C. Chen, C.-Y. Wei, S.-J. Chen, H.-L. Lu, and M. Z. Lee, *Chem. Phys. Lett.*, 1997, **280**, 134.
26. P.-T. Chou, G.-T. Wei, C.-H. Lin, C.-Y. Wei, and C.-H. Chang, *J. Am. Chem. Soc.*, 1996, **118**, 3031.
27. P.-T. Chou, Y.-C. Chen, C.-Y. Wei, S.-J. Chen, H.-L. Lu, and T. H. Wei, *J. Phys. Chem. A*, 1997, **101**, 8581.
28. P.-T. Chou, Y.-C. Chen, and C.-Y. Wei, *Chem. Phys. Lett.*, 1998, **294**, 579.

Received September 14, 2006;
in revised form December 6, 2006