Chemiluminescence of oxygen-free acetone solutions of dimethyldioxirane*

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The decomposition of dimethyldioxirane (**1**) in oxygen-free acetone solutions (46 °C) is accompanied by chemiluminescence (CL) in the visible spectral region. The emitter of CL is triplet-excited methyl acetate (**2***(T)). For the decomposition of solutions of **1** in acetone and deuterated dimethyldioxirane in acetone-D_6 the decay of CL follows the first-order kinetics, and the kinetic isotope effect is observed. Two mechanisms of the formation of **2***(T) are discussed: (*a*) chain-radical process and (*b*) isomerization of **1** to **2**.

Key words: organic peroxides, dimethyldioxirane, chemiluminescence, mechanism of chemiluminescence.

Formation of excited products in the decomposition accompanied by chemiluminescence (CL) is a general property of several cyclic peroxides. For example, the decomposition of dioxetanes gives ketones in singlet and triplet excited states,[1,2] and the decomposition of some ozonides results in the formation of singlet oxygen.[3,4] In the majority of cases, these are precisely the products which are emitters of the luminescence appeared. Cyclic peroxides (dioxiranes[5,6]) are not exceptions in this series. The energy released in the decomposition of dioxiranes to the corresponding ester is equal to ~80 kcal mol^{-1} and, hence, a chemiluminescence process is possible.[5,7] In fact, we have shown[8] that the thermal decomposition of dimethyldioxirane (**1**) in the presence of an activator of CL, 9,10-dibromoanthracene (DBA), results in the appearance of CL caused, as we supposed, by the energy transfer from triplet-excited methyl acetate (**2***(T)) (the main product of the decomposition of **1**) to DBA. Later,[9] we observed a substantially more intense CL in the decomposition of compound **1** sorbed from the gas phase on the surface of Silipor. However, no CL was observed in a solution of **1** in acetone. We related this fact to the quenching process and, first of all, to the presence of oxygen, an efficient quenching agent of triplet-excited states. In this work, we first report on CL in the thermal decomposition of oxygen-free solutions of **1** in acetone.

Experimental

Dioxirane **1** was obtained and analyzed as described in Ref. 10. The kinetics of the decomposition of **1** was monitored spectrophotometrically in a thermostated quartz cell (the optical path was 1 cm) by the decrease in the optical density at λ 335 nm (ε 10 L mol^{-1} cm^{-1})[10] on a Specord M-40 instrument (Carl Zeiss, Jena). Chemiluminescence was monitored on an installation of an FEU-140 photomultiplier calibrated in absolute units according to a procedure described previously.[11] Phosphorescence spectra of methyl acetate (**2**) were recorded on a Hitachi MPF-4 spectrofluorimeter at 77 K. Oxygen from a solution of **1** in acetone was removed by subsequent "freezing—evacuating—thawing out" procedures repeated 5—6 times until the release of gas bubbles stopped completely. After this, a solution of **1** in acetone was placed in a thermostated cell arranged above the photocathode of the photomultiplier, and CL was detected. The volume of the solution studied was 1.5—2 mL.

Results and Discussion

The thermal decomposition (46 °C, $[\mathbf{1}]_0$ = 0.082 mol L^{-1}) of oxygen-free solutions of **1** in acetone resulted in the appearance of CL in the visible spectral region. The maximum intensity of CL was $9.5 \cdot 10^6$ photon s^{-1} mL^{-1}. The spectral composition of the luminescence observed was estimated by boundary light filters and it corresponded to the phosphorescence spectrum of **2** (λ_{max} = 390 nm), which is the emitter of CL detected. The decay of CL is described by a first-order equation (correlation coefficient $r \approx 0.99$). The spectrophotometric analysis of the reaction mixture showed that compound **1** has completely decomposed by the time the luminescence stopped. An analogous character of the luminescence decay (the maximum intensity was $9.6 \cdot 10^6$ photon s^{-1} mL^{-1}) was also observed in the case of thermolysis of an oxygen-free solution of deuterated dimethyldioxirane ($\mathbf{1}_D$) in deuteroacetone ($[\mathbf{1}_D]_0$ = 0.1 mol L^{-1}, 46 °C). It has been previously established[12] that solutions of $\mathbf{1}_D$ in deuteroacetone are more stable. As follows from our data, this is valid for solutions of **1**: the kinetic isotope effect $k^{eff}{}_H/k^{eff}{}_D$ = 3.12, where

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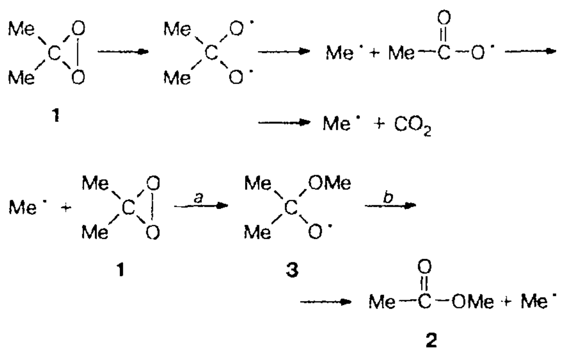
* Dedicated to Prof. W. Adam on the occasion of his 60th birthday.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 477—479, March, 1997.

$k^{\mathrm{eff}}_{\mathrm{H}} = 8.5 \cdot 10^{-3}$ s^{-1}; $k^{\mathrm{eff}}_{\mathrm{D}} = 2.7 \cdot 10^{-3}$ s^{-1}. The light sum (S) of CL of the reaction in the decomposition of **1** and $\mathbf{1}_{\mathrm{D}}$ is equal to $3.6 \cdot 10^{-15}$ and $9.1 \cdot 10^{-15}$ Einstein, respectively. Therefore, the CL yield ($\varphi_{\mathrm{CL}} = S \cdot [\mathbf{1}]_0^{-1}$) is equal to $2.2 \cdot 10^{-11}$ and $6 \cdot 10^{-11}$ Einstein mol^{-1} for **1** and $\mathbf{1}_{\mathrm{D}}$, respectively.

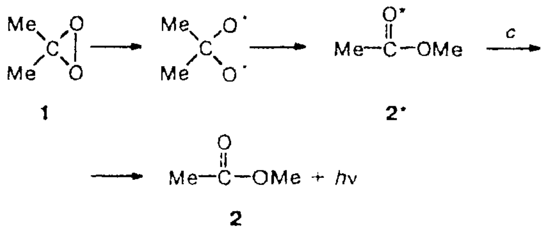
For comparison, we performed thermolysis of solutions of **1** in acetone at the same temperature, but in the presence of oxygen. It turned out that the complete decomposition of **1** in oxygen-free solutions is ~4 times faster, which agrees well with the published data.[13] According to Ref. 13, compound **1** is consumed in the chain-radical process. The chain reaction is inhibited in an atmosphere of O_2, which explains the retardation of the decomposition rate of **1**:

Scheme 1



Taking into account the chain-radical character of the decomposition of **1**, it is reasonable to assume that the luminescence appears due to the recombination of the peroxide radicals (see Ref. 14) upon the thermolysis of **1** in the presence of O_2. However, we observed CL in the oxygen-free solutions. The enthalpy of reaction (*b*) (see Scheme 1) was calculated from the heats of formation ($\Delta_f H^0$) of the reagents ($\Delta_f H^0(\mathbf{2}) = -97.9$ kcal mol^{-1},[15] $\Delta_f H^0(\mathrm{CH_3}^{\cdot}) = 34.8$ kcal mol^{-1},[16] and $\Delta_f H^0(\mathrm{RO}^{\cdot}) = -57.3$ kcal mol^{-1} [*]) and is equal to -5.8 kcal mol^{-1}. This is insufficient for the appearance of CL. The heat of reaction (*a*) calculated similarly taking into account $\Delta_f H^0(\mathbf{1}) = -21.8$ kcal mol^{-1} (calculated by the Benson method[18]) is equal to -70.3 kcal mol^{-1}. If $\mathbf{2}^*$(T) is formed in the sequence of reactions (*a*) and (*b*), it is necessary to assume the formation of **3** in the electron-excited state, whose lifetime should be equal to at least 10^{-9} s. In addition, the activation enthalpy of reaction (*b*) should be not less than 15 kcal mol^{-1} to fulfill the condition for the formation of the excited product, *i.e.*, $\Delta H^0 + \Delta H^* \geq E_t^*$ ($E_t^*(\mathbf{2}) = 90$ kcal mol^{-1}).[5] When these conditions are fulfilled, the formation of $\mathbf{2}^*$(T) and the appearance of CL caused by reactions (*a*) and (*b*) are possible. However, in our opinion, another mechanism of the appearance of luminescence is preferable: the isomerization of **1** to **2** probably occurs *via* a biradical intermediate (Scheme 2).

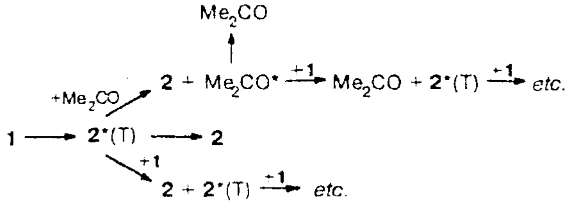
Scheme 2



As mentioned above, the energy released in this process is quite enough for the formation of $\mathbf{2}^*$(T) and, hence, for the appearance of CL. In terms of this mechanism of generation of luminescence and taking into account that **1** is consumed in the chain-radical process (see Scheme 1), it can be supposed that the decomposition of **1** in oxygen-free solutions is caused by the simultaneous reactions shown in Schemes 1 and 2. This is precisely reaction (*c*) (see Scheme 1) that is chemiluminescent. In the absence of oxygen, its contribution is most likely small, which explains the relatively low intensity of the detected CL. In the presence of oxygen in solution, when the chain process is inhibited, isomerization of **1** (Scheme 2) also occurs, but quenching of $\mathbf{2}^*$(T) by oxygen does not allow one to detect chemiluminescence.

The fact that the isomerization of **1** results in the formation of $\mathbf{2}^*$(T) is additionally confirmed by the existence of phosphorescence (PS) induced by the excitation of a frozen solution of **1** at its absorption band (Fig. 1). The spectrum of the PS observed consists of the PS bands of **2** and acetone ($\mathrm{Me_2CO}$), and the dynamics of their change depending on the duration of irradiation of exciting light testifies that triplet-excited acetone ($\mathrm{Me_2CO^*}$(T)) appears due to the energy transfer from $^3\mathbf{2}^*$(T). Thus, taking into account the aforementioned facts, one more possible channel of decomposition of **1** can be supposed: *via* the mechanism of quantum-chain processes that is realized in decomposition of 1,2-dioxetanes[19] (Scheme 3).

Scheme 3



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[*] Calculated from the equation taken from Ref. 17: $\Delta_f H^0(\mathrm{RO}^{\cdot}) = \Delta_f H^0(\mathrm{ROH}) + 52$ kcal mol^{-1}, where $\Delta_f H^0(\mathrm{ROH}) = -109.2$ kcal mol^{-1} (obtained by the additivity method for thermochemical increments).[18]

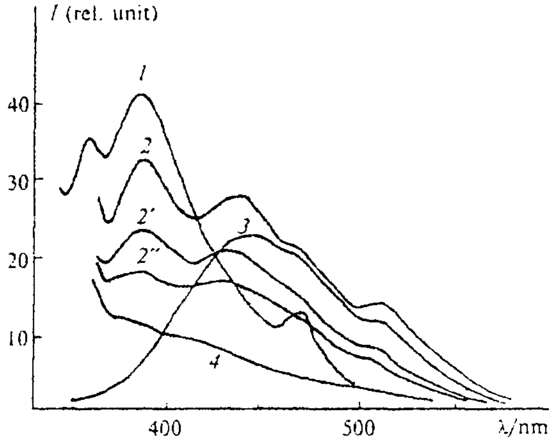

Fig. 1 Phosphorescence spectra (recorded at 77 K): *1*, methyl acetate (λ_{exc} 260 nm, C = 0.09 mol L^{-1} in MeCN); *2*, *2'*, and *2''*, dimethyldioxirane (λ_{exc} 350 nm, C = 0.09 mol L^{-1} in acetone, spectra *2'* and *2''* were recorded under continuous irradiation 25 min apart); *3* and *4*, acetone (λ_{exc} 320 (*3*), 350 nm (*4*)).

This mechanism, as well as the chain-radical mechanism, explains satisfactorily the effect of oxygen on the decomposition of **1**: oxygen quenches molecules of triplet methyl acetate, thus inhibiting the quantum-chain process. The chain-radical mechanism of the decomposition of **1** can be considered to be more or less justified, while the role of quantum-chain processes in the decomposition of **1** should be studied further.

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Received October 1, 1996