Photolysis of dimethyldioxirane

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Phosphorescence of methyl acetate formed by isomerization of electron-excited dimethyldioxirane is observed upon excitation at the wavelength of the absorption band of dimethyldioxirane in acetone at 77 K. The quantum yield of the photodecomposition of dimethyldioxirane at 296 K is equal to 13.1±0.7 mol Einstein^{-1}. The high quantum yield of photolysis is evidence for the chain mechanism of decomposition of dimethyldioxirane.

Key words: dimethyldioxirane, photolysis, quantum yield; phosphorescence.

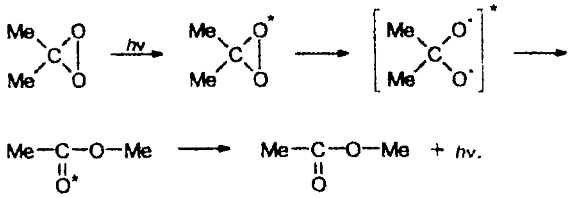
Dioxiranes (three-membered cyclic peroxides) are a relatively new class of oxidizing reagents that are used for preparing oxygen-containing compounds.[1–5] Reactions involving dioxiranes have been widely and successfully studied, especially after pure solutions of dioxiranes were obtained.[6,7] Spontaneous isomerization of dioxirane to the corresponding ester is a strongly exothermic process ($\Delta H \approx -80$ kcal mol^{-1}), and the energy released in this reaction is enough for the formation of a product in the electron-excited state.[2,4] It has been shown previously[8] that the thermolysis of dimethyldioxirane (**1**) in the presence of 9,10-dibromoanthracene is accompanied by chemiluminescence (CL) caused by the radiative deactivation of the excited activator formed by the transfer of energy from triplet methyl acetate $(2^*)^T$. This fact indicates some general properties of dioxiranes and four-membered peroxides — 1,2-dioxetanes — whose decomposition also results in the formation of excited carbonyl compounds.[9] Upon photolysis of dioxetanes, excited products are formed in yields close to unity. Dioxiranes are also prone to transformations under the action of the light.[10–16] As shown previously,[10,11] irradiation of a solution of methyl(trifluoromethyl)dioxirane with light at λ = 250—380 nm results in its decomposition *via* a chain-radical mechanism. At the same time, quantitative data on photolysis of dioxiranes are lacking. The present work is aimed at the determination of the quantum yield of the photolysis of compound **1** at different wavelengths of the exciting light.

Experimental

Dioxirane **1** was obtained as described previously.[7] Compound **1** was identified by ^{13}C NMR spectroscopy on a Bruker AM 300 spectrometer (the signal of the C atom bound to the peroxide group at δ 102.35 is characteristic) and spectrophotometrically on a Specord M 40 spectrophotometer (λ_{max} = 335 nm, ε = 10 L mol^{-1} cm^{-1}).[7] The kinetics of photolysis were monitored by the decrease in the optical density of dioxirane **1** at λ = 340 nm. Photolysis was performed in the cell compartment of a Hitachi MPF-4 fluorimeter by monochromatized light ($\Delta\lambda$ = ±5 nm) from a xenon lamp. The intensity of the light beam at different wavelengths of the exciting light (determined by a ferrioxalate actinometer[17]) was equal to $3.2 \cdot 10^{14}$, $3.5 \cdot 10^{14}$, and $3.9 \cdot 10^{14}$ photon s^{-1} at λ_{exc} = 340, 350, and 360 nm, respectively. For irradiation, a solution of dioxirane **1** (2.7 mL) was placed in a cell with an optical pathlength of 1 cm.

Results and Discussion

Continuous irradiation of a solution of dioxirane **1** in acetone frozen at 77 K results in the appearance of phosphorescence (PS) in the region of its absorption. The phosphorescence spectrum as well as the excitation spectra of pure acetone and of a solution of **1** are presented in Fig. 1. The comparison of these spectra with the absorption spectrum of compound **1** (Fig. 2) shows that PS of dioxirane **1** appears upon excitation at its absorption band. The maximum in the PS spectrum of dimethyldioxirane **1** at 385 nm corresponds to PS of methyl acetate **2** and is likely caused by the following process:



The formation of esters upon irradiation of dioxiranes has been observed previously.[10,12–16] For example, phenyl benzoate and phenyl trifluoroacetate are obtained by the irradiation of diphenyldioxirane and phenyl(trifluoromethyl)dioxirane, respectively, in matrices at 10 K.[13,15,16] However, no data on PS during isomerization of dioxiranes has been reported.

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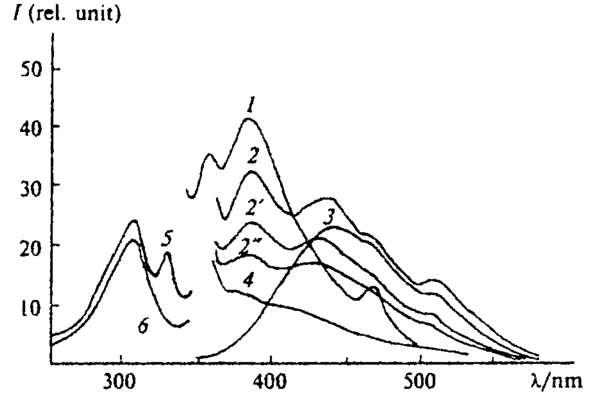


Fig. 1. Phosphorescence spectra at 77 K: *1*, methyl acetate **2** (λ_{exc} = 260 nm, [**2**] = 0.09 mol L^{-1}, in MeCN); *2*, *2'*, and *2''*, dimethyldioxirane **1** (λ_{exc} = 350 nm, [**1**] = 0.09 mol L^{-1}, in acetone), spectra *2'* and *2''* were recorded at constant irradiation at an interval of 25 min; *3* and *4*, acetone (λ_{exc} = 320 nm (*3*) and 350 nm (*4*)). Excitation spectra: *5*, dimethyldioxirane **1** (λ_f = 380 nm, [**1**] = 0.09 mol L^{-1}, in acetone); *6*, acetone (λ_f = 380 nm).

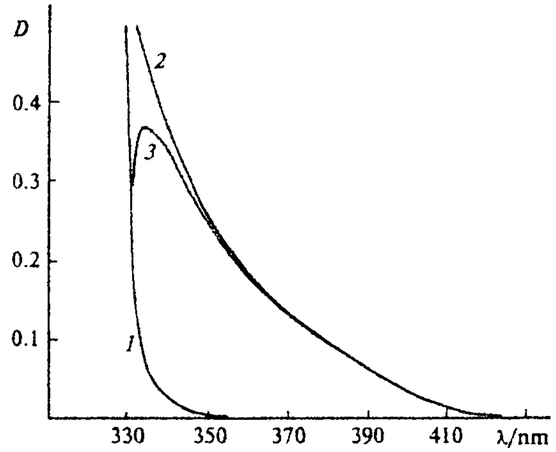
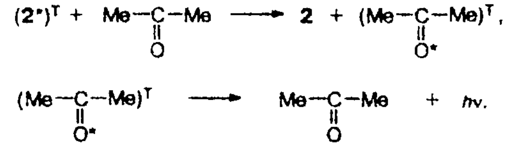


Fig. 2. Absorption spectra (296 K, *l* = 1 cm): *1*, acetone (relative to water); *2* and *3*, solution of dimethyldioxirane **1** in acetone ([**1**] = 0.035 mol L^{-1}, relative to air (*2*) and relative to acetone (*3*)).

It is known that excited states of cyclic peroxides are dissociative.[9,18] For example, the triplet and singlet states of tetramethyldioxetane are much higher in energy than the activated transition state in the reaction of thermal decomposition and correlate in symmetry and spin with the excited states of the products (ketones). It is likely that a similar situation occurs in the case of dioxiranes. According to the published data,[19] the energy of the lower excited state of dioxiranes (E^*) is equal to ~94 kcal mol^{-1} (which corresponds to the electronic transitions in the UV spectral region). Since the change in enthalpy for the decomposition of dioxirane is equal to ~75–80 kcal mol^{-1}, the total energy released during the decomposition of excited dioxirane **1** is much higher than the energy of the excited state of **2**, and hence, the formation of $(\mathbf{2}^*)^T$ is possible. This is confirmed by our experimental data. The observed PS of compound **2** testifies that $(\mathbf{2}^*)^T$ is formed in an adiabatic process similar to that observed in the case of photochemical transformations of solutions of 1,2-dioxetanes.[18]

In addition to the maximum indicated, the PS spectrum of dioxirane **1** contains a component assigned by us to PS of acetone (see Fig. 1). The decrease in the intensity of PS during irradiation testifies that photolysis of dioxirane **1** occurs in the frozen solution. The parallel changes in PS of compound **2** and Me_2CO are evidence for the formation of triplet-excited acetone $(Me_2CO^*)^T$ due to the transfer of energy from ester **2**.



$$(\mathbf{2}^*)^T + \mathrm{Me{-}\underset{\overset{\|}{O}}{C}{-}Me} \longrightarrow \mathbf{2} + (\mathrm{Me{-}\underset{\overset{\|}{O^*}}{C}{-}Me})^T,$$

$$(\mathrm{Me{-}\underset{\overset{\|}{O^*}}{C}{-}Me})^T \longrightarrow \mathrm{Me{-}\underset{\overset{\|}{O}}{C}{-}Me} + h\nu.$$

Thus, the photolysis of dioxirane **1** in frozen solutions results in the formation of $(\mathbf{2}^*)^T$ and $(Me_2CO^*)^T$, which can participate in the photochemical transformations of compound **1** in solution. The photolysis of compound **1** at room temperature (296 K) was studied at 340, 350, and 360 nm. These wavelengths were chosen for the purpose of the selective excitation of dioxirane **1** in the region where the absorption of acetone is absent (see Fig. 2). The initial concentration of compound **1** was ~0.035 mol L^{-1} in all experiments. The kinetics of the photolysis of dioxirane **1** can be described by the following equation:

$$-d[\mathbf{1}]/dt = \varphi v, \qquad (1)$$

where [**1**]/mol L^{-1} is the concentration of dioxirane **1**, v is the rate of light absorption by dioxirane per unit volume; and φ is the quantum yield of the photoreaction. The rate of light absorption can be written in the following form

$$v = IV^{-1} = I_0(1 - 10^{-\varepsilon[\mathbf{1}]l})V^{-1}, \qquad (2)$$

where V/L is the irradiated volume; I_0/Einstein s^{-1} is the incident light intensity; l/cm is the optical pathlength; and ε/L mol^{-1} cm^{-1} is the extinction coefficient of the solution of **1** at the wavelength of the exciting light. Inserting Eq. (2) in Eq. (1) and integrating it taking into account that $D = \varepsilon[\mathbf{1}]l$, we obtain

$$[\mathbf{1}] = [\mathbf{1}]_0 - \varphi(I_0V^{-1})\int_{t=0}^{t}(1 - 10^{-D})dt = [\mathbf{1}]_0 - \varphi Q. \qquad (3)$$

The value $Q = (I_0V^{-1})\int(1 - 10^{-D})dt$ is the dose of absorbed light, which is determined by numerical integration.

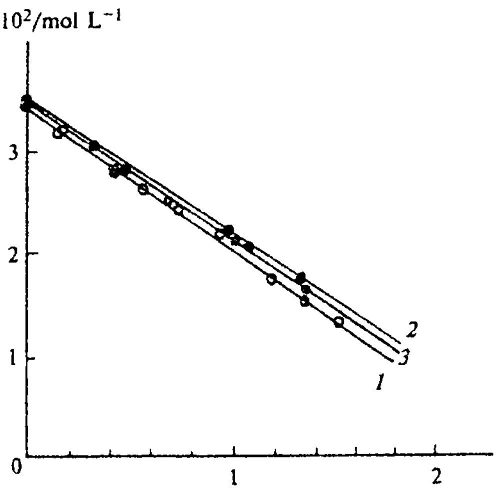
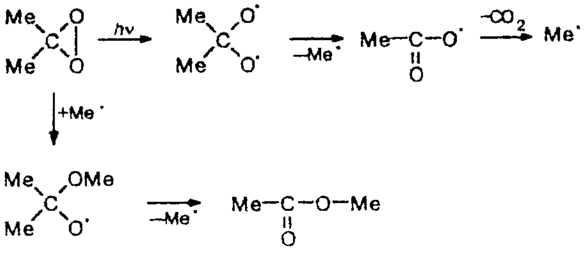


Fig. 3. Kinetics of photolysis of dimethyldioxirane at λ_{exc} = 340 (*1*), 350 (*2*), and 360 nm (*3*) in coordinates of Eq. (3) at 296 K.

The dependences of the consumption of dioxirane **1** on the dose of the exciting light at different wavelengths are presented in Fig. 3. As can be seen, the kinetics of the photolysis obey Eq. (3). Based on the data presented in Fig. 3, we obtained the following values: φ = 13.9±0.6, 12.9±1.7, and 13.1±0.7 mol Einstein^{-1} at λ_{exc} = 340, 350, and 360 nm, respectively. Thus, the quantum yield of the photolysis of compound **1** is independent of the wavelength and much higher than unity. The latter result is evidence for the chain mechanism of the decomposition of dioxirane **1**.

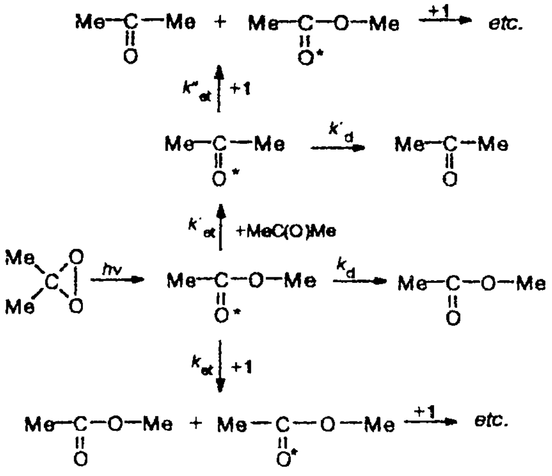
Based on a study of the products of the photolysis of methyl(trifluoromethyl)dioxirane,[10] it was concluded that dioxiranes react with the $CH_3^{\cdot}$ and $CF_3^{\cdot}$ radicals, and α-alkoxy-substituted radicals are formed as intermediates. Therefore, the high quantum yield of the photolysis of dioxirane **1** is probably caused by its chain-radical decomposition *via* a scheme similar to that proposed previously[20] for the thermal decomposition of compound **1** (Scheme 1).

Scheme 1



However, since triplet-excited methyl acetate $(\mathbf{2}^*)^T$ is formed in the photolysis of dioxirane **1**, the high quantum yield of the decomposition of compound **1** can also be explained by its consumption in a chain process, in which the reaction of **1** with $(\mathbf{2}^*)^T$ and $(Me_2CO^*)^T$ plays a key role (Scheme 2).

Scheme 2



The decomposition of dioxirane **1** *via* this mechanism is characteristic of the photolysis of dioxetanes, because the quantum yield of their photodecomposition can attain 200.[18] The quantum yield of the photolysis of compound **1** depends on the energy transfer constant (k_{et}), the deactivation constants of $(\mathbf{2}^*)^T$ and Me_2CO^* (k_d), and the chain length (η). The η value can be roughly estimated assuming that $k_{et} = k'_{et} = k''_{et} \approx 10^{10}$ L mol^{-1} s^{-1} and is close to the diffusion-controlled constant, and that $k_d \approx k'_d \approx 10^6-10^7$ s^{-1} (see Ref. 21). Then the chain length $\eta = (k_{et} \cdot [\mathbf{1}]) \cdot k_d^{-1} \approx 30$. It is most probable that both chain mechanisms of decomposition of dioxirane **1** occur simultaneously. The elucidation of the contributions of the routes of the decomposition of compound **1** requires further experiments.

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