Chemiluminescence and catalysis of decomposition of dimethyldioxirane adsorbed from the gas phase on silipore containing tris(bipyridyl)ruthenium complex $Ru(bpy)_3Cl_2$ and 9,10-diphenylanthracene*

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The kinetics of decomposition of dimethyldioxirane (DMD) adsorbed from the gas phase on the silipore surface was studied by the chemiluminescence (CL) technique. The lower boundary of the CL yield in the reaction of DMD decomposition ($4 \cdot 10^{-9}$ Einstein mol^{-1}) and chemiexcitation yield of methyl acetate ($4 \cdot 10^{-4}$) were estimated. Chemiluminescence upon decomposition of DMD on the silipore surface in the presence of activators of CL such as tris(bipyridyl)ruthenium complex $Ru(bpy)_3Cl_2$ and 9,10-diphenylanthracene was revealed. $Ru(bpy)_3Cl_2$ activates the luminescence according to chemically induced electron exchange mechanism.

Key words: chemiluminescence, mechanism of chemiluminescence, dimethyldioxirane, gas phase, silipore, tris(bipyridyl)ruthenium complex, catalysis.

In recent years, dioxiranes have attracted the attention of researchers due to their surprising oxidation properties.[1—7] These three-membered cyclic peroxides are very efficient reagents for highly-selective oxidation of various classes of organic compounds such as alkanes, alkenes, and compounds containing heteroatoms. However, recent studies showed that processes of some transformations of dioxiranes are accompanied by chemiluminescence (CL). The possibility of CL has been assumed previously[3,4,8] and then confirmed experimentally.[4,9—11] Almost all known chemiluminescence reactions of dioxiranes were studied mainly in solution. At the same time, it is evident that processes resulting in the formation of products in the electron-excited state can also occur on the sorbent surface. For example, it is known that the surface significantly enhances CL accompanying the decomposition of such peroxides as dioxetanes rather than catalyzes their decomposition.[12—16] Some changes in the chemiluminescence behavior of cyclic peroxides can be expected when their reactions are transferred from solution to the surface. In fact, we have recently shown[17] that isomerization of dimethyldioxirane (DMD) (the most abundant representative of the class of dioxiranes) sorbed from the gas phase on the silipore surface is accompanied by rather intense CL. The DMD_{ads}—silipore system is very attractive fof studying due to the high intensity of CL and the absence of "dark" reactions impeding the study of CL of dioxirane in solution (induced decomposition,[18—21] catalysis by admixtures,[22] *etc.*). In this work, we consider the kinetics of CL during the decomposition of DMD sorbed from the gas phase on the silipore surface and report on a significant enhancement of CL in the presence of tris(dipyridyl)ruthenium complex $Ru(bpy)_3Cl_2$ (Ru^{II}) and 9,10-diphenylanthracene (DPA) supported on the silipore surface.

Experimental

Chemiluminescence was detected using an FEU-140 photomultiplier with a maximum of spectral sensitivity at 415 nm on a photometric installation calibrated in absolute units by a reference radiation source based on a scintillator containing the radioactive ^{14}C isotope according to the previously described method.[23] The spectral sensitivity of the photocathode was determined by a strip-like SIRSh-6-100 tungsten lamp and a set of interference light filters in the region of 365—670 nm. The photosensitivity of the photocathode in the region of Ru^{II} luminescence (λ_{max} = 630 nm) was 5% of the maximum value in the region of 410—420 nm. Chemiluminescence spectra were recorded using boundary light filters. The phosphorescence spectrum of triplet methyl acetate ($MA^*(T)$) (λ_{max} = 390 nm)[24] was recorded on a Hitachi MPF-4 spectrofluorimeter at 77 K.

Chemiluminescence was detected using a setup shown in Fig. 1. A solution (2 mL) of DMD in acetone ($[DMD]_0 = 6 \cdot 10^{-2}$ mol L^{-1}) was placed in a cell connected through a glass adapter with the second 27-mL cell containing silipore (100 mg) (Silipore 400, Chemapol, 0.125—0.160 mm, 400 m^2 g^{-1}) and arranged above the photocathode of FEU. An argon flow admitting through the capillary to the first cell

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* Devoted to Prof. R. W. Murray on his 70th birthday.

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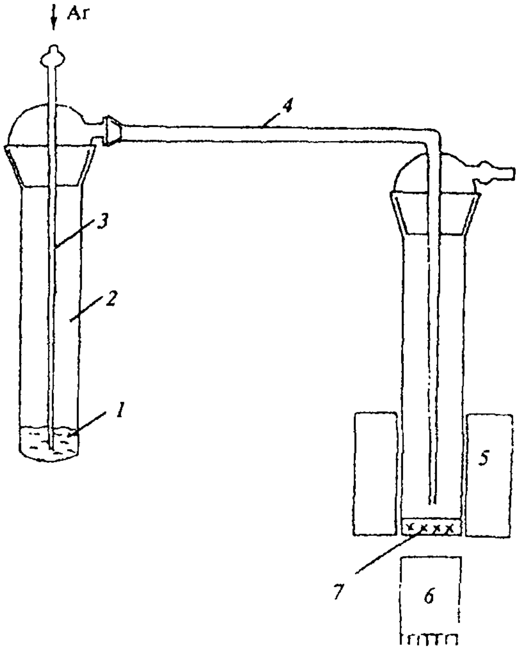


Fig. 1. Setup designed for detection of CL: *1*, solution of DMD in acetone; *2*, cell containing a solution of DMD in acetone; *3*, capillary for admission of argon; *4*, glass adapter; *5*, thermostatted jacket; *6*, FEU-140; and *7*, cell containing silipore.

captured acetone vapor from DMD, and the vapor fell in the second cell thermostatted at a specified temperature. This procedure lasted for ~1 min. Then the argon admission was stopped, and the CL spectrum was recorded in the static regime. Chemiluminescence in the presence of activators was detected similarly by the application of the corresponding amount of activators on the silipore surface.

Diphenylanthracene and Ru^{II}, which were used as the activators of CL, were supported onto silipore as follows. The corresponding amount of silipore was placed in a solution of activators in acetonitrile. The suspension obtained was stirred for 15 min, and the solution was decanted. The activators were completely sorbed on the support. The suspension was dehydrated *in vacuo* (10^{-2} Torr).

Dimethyldioxirane was prepared and analyzed according to the known procedure.[25]

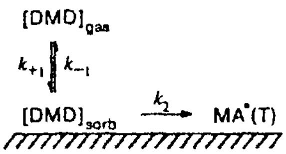
Results and Discussion

The luminescence decay reflecting the decomposition of the sorbed dioxirane, which is observed after the end of the argon admission to a cell with DMD, obeys a first-order law. As was shown by the boundary light filters, MA*(T) is the emitter of luminescence. The maximum intensity of CL is $5.7 \cdot 10^6$ photon s^{-1} (75 °C). The rate constants of CL (k_{CL}) obtained at different temperatures from the semilogarithmic anamorphoses of the kinetic curves of CL decay are presented below.

T/°C	65	75	85	90
$k_{CL} \cdot 10^2/s^{-1}$	1.2	0.9	0.9	1.0

It is seen that the rate of the process is virtually temperature-independent. This is most likely related to the fact that the activation energy is the effective value, since, according to Scheme 1, the k_{CL} value depends on the sorption—desorption of DMD along with the isomerization of dioxirane to methyl acetate.

Scheme 1



It follows from analysis of Scheme 1 that the reaction rate (w) is determined by the expression

$$w = k_2k_{+1}[DMD]_{gas}/(k_{-1} + k_2),$$

$$k_{CL} = k_2k_{+1}/(k_{-1} + k_2).$$

The increase in the desorption rate of DMD from the silipore surface (k_{-1}) with temperature increase seems to compensate for the increase in k_2, the k_{CL} value remaining almost unchanged.

In the presence of silipore-supported Ru^{II}, a significant enhancement of CL is observed. For example, at 75 °C and $[Ru^{II}] = 1 \cdot 10^{-6}$ mol g^{-1}, the maximum intensity of luminescence increases by two orders of magnitude. The kinetic curve of CL decay, the maximum of which corresponds to the luminescence of the ruthenium complexes, consists of two exponential regions corresponding to the fast and slow decays (Fig. 2).

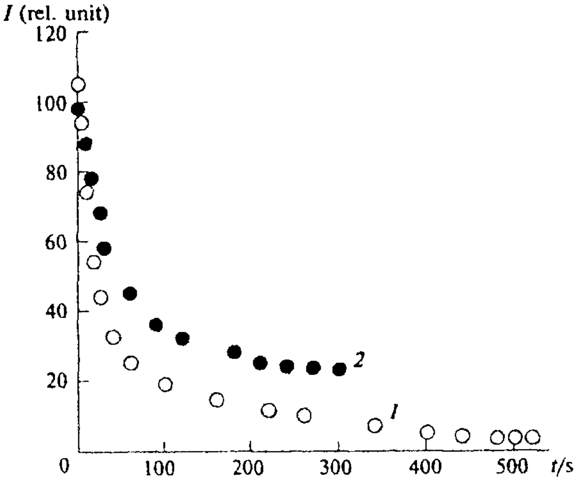


Fig. 2. Typical kinetic curves of CL decay during the decomposition of DMD sorbed from the gas phase on the silipore surface in the presence of silipore-supported activators of CL: at $J = 10$, $[Ru^{II}]_0 = 0.5 \cdot 10^{-6}$ mol g^{-1} (*1*) and $J = 5$, $[DPA]_0 = 1 \cdot 10^{-6}$ mol g^{-1} (*2*). $T = 75$ °C, J is the relative sensitivity of the device.

We believe that this is precisely the decomposition of DMD which corresponds to the fast region of the kinetic curve of CL decay. The luminescence in the slow region is most likely caused by the thermal decomposition of a labile compound formed in the oxidation of the complex by dioxirane.

The temperature dependences of the observed rate constants (k'_{CL}) obtained from semilogarithmic anamorphoses of the kinetic curves of luminescence decay in the presence of Ru^{II} ($[Ru^{II}]_0 = 5 \cdot 10^{-6}$ mol g^{-1}) in the first exponential region are presented below.

T/°C	55	66	70	75	80	85	90
$k'_{CL} \cdot 10^2$/s^{-1}	3.2	4.8	6.1	6.6	7.1	7.4	8.2

It is found from the temperature dependences of k'_{CL} that

$$\log k'_{CL} = (3.0\pm0.5) - (6.0\pm0.8)/\theta \ (r = 0.96),$$

where $\theta = 2.303RT$ kcal mol^{-1}. These activation parameters, as those for the decomposition of DMD on the surface of nonactivated silipore, are most likely also effective values reflecting the complex totality of transformations of DMD on silipore in the presence of Ru^{II} supported on the surface.

As follows from Fig. 3, k'_{CL} depends linearly on the concentration of Ru^{II}. Therefore, $k'_{CL} = a + b[Ru^{II}]$. According to the data in Fig. 3, it was found that $a = (1.7\pm0.6) \cdot 10^{-2}$ and $b = (9.6\pm1.8) \cdot 10^3$, where a and b are the effective parameters. It is seen that Ru^{II} accelerates the decomposition of DMD rather than increasing the luminescence intensity.

Using some assumptions, we can estimate (from the data obtained) the lower boundary of the CL yield for the decomposition of DMD sorbed from the gas phase on the silipore surface. Since dimethyldioxirane exists in solution only in a mixture with acetone,[1–7] and a solution of DMD in acetone is distilled virtually without fractionation (most likely, due to the solvation effect[2]), the corresponding data on elasticity or pressure of its vapor are not available. However, we can assume the pressures of acetone and DMD vapors to be approximately equal (177 Torr).[26] Based on this fact and taking into account that the velocity of argon admission was 10 mL min^{-1}, we calculated the content of DMD in the gas phase in the cell with silipore: $2.8 \cdot 10^{-7}$ mol. Since the light output of the decomposition of DMD_{ads} on silipore at 75 °C was $7 \cdot 10^8$ photon, the CL yield is $\eta_{CL} = S/[DMD_{ads}] \geq 4 \cdot 10^{-9}$ Einstein mol^{-1}. The CL yield on the silipore surface is two orders of magnitude higher than the value obtained by us previously when the decomposition of DMD in deoxygenated acetone was studied.[10] This is quite reasonable, because it is known that the radiative efficiency of excited molecules in the triplet state increases on the sorbent surface.[27] In addition, CL is favored by a considerable decrease in the efficiency of quenching by the solvent and various admixtures that are present in the solution. However, in our opinion, there is another reason for the increase in the luminescence yield on silipore, which is in the mechanism of decomposition of DMD. Let us consider possible routes leading to MA*(T). It can be assumed that the formation of MA*(T) occurs due to the following reaction:

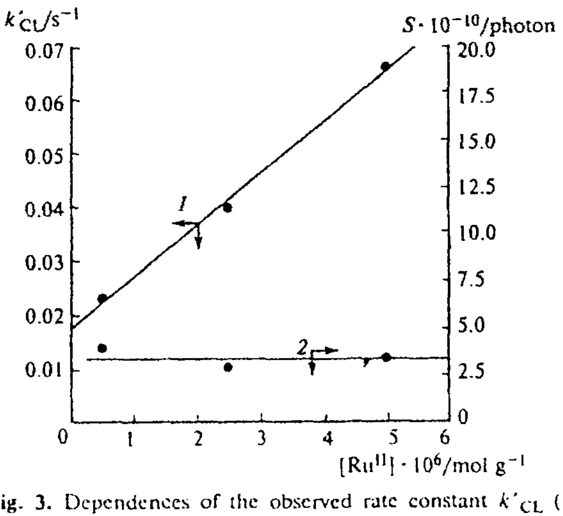
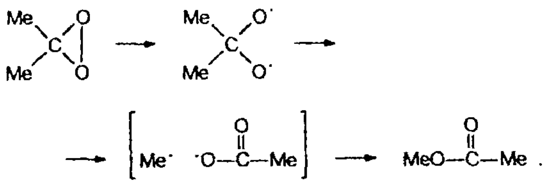


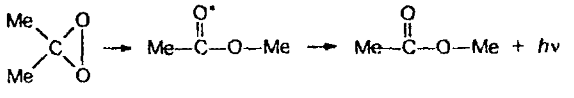
Fig. 3. Dependences of the observed rate constant k'_{CL} (*1*) and light output of the decomposition of DMD_{ads} (*S*) (*2*) on the silipore surface on the concentration of Ru^{II} (75 °C).



The heat released in the recombination of the geminal radical pair and calculated from the heats of formation of the participants of the reaction is $\Delta H^\circ = 83.1$ kcal mol^{-1}. On the other hand, the activation energies of these reactions are usually low (lower than 5 kcal mol^{-1}). Taking into account that the energy of MA in the triplet state is ~90 kcal mol^{-1} (see Refs. 3, 4, and 8), we can conclude that the synthesis of MA*(T) *via* the scheme indicated is improbable.

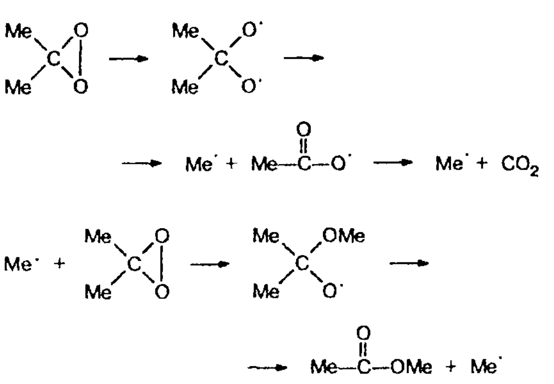
Another and main chemiluminescence channel is, in our opinion, the isomerization reaction (Scheme 2).

Scheme 2



The energetics of this reaction assumes the formation of MA in the triplet state, since the enthalpy of this reaction >85 kcal mol^{-1} and the activation energy is ~15—20 kcal mol^{-1} (see Refs. 3, 4, and 8). The third possibility considered is the synthesis of MA*(T) due to the decomposition of DMD *via* the chain radical mechanism[20] (Scheme 3).

Scheme 3



However, as we have shown previously,[10] this route cannot result in CL because of energy concepts. Nevertheless, this is the chain radical mechanism which is predominant in the consumption of dioxirane in the solution, and the contribution of the isomerization reaction to CL (see Scheme 2) is very insignificant. On the sorbent surface, the decomposition of DMD *via* the chain radical mechanism is not so efficient, and the main contribution to its decomposition is made by the isomerization to MA accompanied by luminescence, which reflects a considerable increase in the CL yield on going from the solution to the heterogeneous system.

It is noteworthy that the estimated value of η_{CL} in the DMD_{ads}—silipore system is the minimum of the possible ones, since it was assumed in the calculation that the all DMD in the cell is sorbed on the sorbent surface. In fact, this fraction may be only several percent and, hence, a considerably higher value of η_{CL} can be expected.

It is known that $\eta_{CL} = \eta^*\eta_{rad}$, where η^* is the excitation yield and η_{rad} is the radiation yield. Data on the radiative efficiency of MA*(T) are unavailable. Therefore, it is not a great error for the estimation of the radiation yield of MA*(T) to compare this value to η_{rad} of related ketones, which is equal to $\sim 10^{-5}$. Therefore, the value of the excitation yield of MA*(T) in the decomposition of DMD on the silipore surface is at least not lower than 10^{-4}. This suggests that a considerably more intense CL can be expected for decomposition of chromophore-containing dioxiranes,[28,29] whose radiation yields from triplet states of the corresponding esters (such as dimesityldioxirane or diphenyldioxirane) are assumed to be substantially higher.

As mentioned above, additions of the silipore-supported Ru^{II} complex enhance substantially the luminescence and catalyze the decomposition of DMD. Since CL reflects the catalytic route of isomerization of DMD, we can write

$$I_{CL} = \eta^*_{Ru}\eta_{FL}k_2[Ru^{II}]_0[\mathbf{1}]_0 \cdot \exp[-(k_1 + k_2[Ru^{II}]_0)t],$$

where η^*_{Ru} is the excitation yield of Ru^{*II} in the reaction, and η_{FL} is the fluorescence yield of the complex. The maximum intensity of CL is determined by the expression

$$I_{CL}{}^m = \eta^*_{Ru}\eta_{FL}k_2[Ru^{II}]_0[\mathbf{1}]_0,$$

and the light output of the reaction is the following:

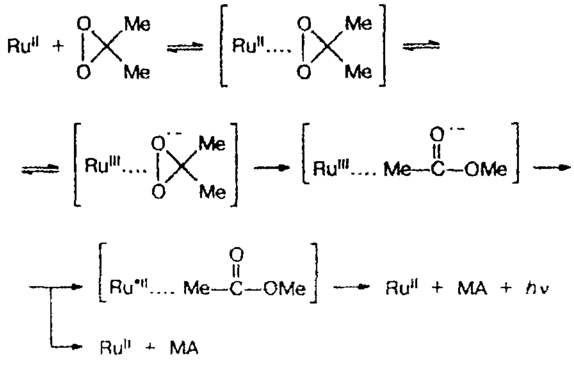
$$\begin{aligned} S &= \int_0^\infty I\mathrm{d}t = \\ &= \eta^*_{Ru}\eta_{FL}k_2[Ru^{II}]_0[\mathbf{1}]_0 \int_0^\infty \exp[-(k_1 + k_2[Ru^{II}]_0)t]\mathrm{d}t = \\ &= \eta^*_{Ru}\eta_{FL}k_2[Ru^{II}]_0[\mathbf{1}]_0(k_1 + k_2[Ru^{II}]_0)^{-1}. \qquad (1) \end{aligned}$$

It follows from the data in Fig. 3 that the light output of the reaction in the first exponential region is almost independent of the concentration of Ru^{II} and equal to $\sim 34 \cdot 10^9$ photon. The CL yield was estimated from Eq. (1): $\eta^*_{Ru}\eta_{FL} = 3 \cdot 10^{-7}$ Einstein mol^{-1}.

It is seen that in the presence of silipore-supported Ru^{II}, the CL yield, as expected, is substantially higher than that in the decomposition of DMD on clean silipore. However, the chemiluminescence yield of Ru^{II} ($3 \cdot 10^{-5}$) is an order of magnitude lower than the corresponding η^* value for MA. It is likely that the increase in the radiation intensity and the CL yield in the decomposition of DMD in the presence of Ru^{II} is due to a higher radiation yield of the complex (0.0095), which is three orders of magnitude higher than η_{rad} of MA.

It can be assumed that the catalysis of dioxirane decomposition and activation of luminescence by silipore-supported Ru^{II} occur *via* the known mechanism of chemically initiated electron exchange luminescence similarly to that occurring in the solution[11] (Scheme 4).

Scheme 4



This mechanism is very probable, because it is known that dioxiranes participate efficiently in electron transfer (ET) processes,[30—32] which agrees well with the theoretically calculated electron affinity for the simplest dioxirane (2 eV).[33]

It is of interest that the yield of CL activated by the Ru^{II} complex during the decomposition of DMD in the solution is approximately three orders of magnitude higher than that on the silipore surface. The last fact is evidently related to the difference in the rates of diffusion of the reagents on going from the homogeneous system to heterogeneous conditions. Since $k_{\rm diff}$ on silipore is considerably lower than $k_{\rm diff}$ in the solution, the probability of collision of Ru^{II} molecules and DMD on the surface decreases, which results in a decrease in the CL yield.

The oxidation of several silica gel-supported polyaromatic hydrocarbons (PAH), such as pyrene, chrysene, *etc.*, by dioxirane from the gas phase has previously been reported.[2,34,35] Based on the results obtained, we can reasonably assume that these reactions should be accompanied by CL. To check this assumption, one of the representatives of the PAH class, DPA, was supported on the silipore surface. In fact, CL is observed during the decomposition of DMD sorbed from the gas phase on the silipore surface in the presence of DPA (DPA is the luminescence emitter). The luminescence intensity in the presence of DPA ($[\mathrm{DPA}] = 1 \cdot 10^{-6}$ mol g^{-1}) increases by an order of magnitude. The kinetic curve of luminescence decay, as in the case of Ru^{II}, consists of two exponential regions corresponding to the fast and slow CL decay (see Fig. 2). It is noteworthy that these regularities of CL are similar to those observed[36] in the thermolysis of DMD in the presence of DPA in the solution. It has been shown previously[36] that the decomposition of dioxirane occurs during the time corresponding to the first exponential region. The further chemiluminescence is caused by the decomposition of a peroxide compound formed in the oxidation of DPA by dioxirane. It is reasonable to assume that the similarity of behavior of CL on silipore is explained by analogous facts. The observed first-order rate constants ($k''_{\rm CL}$) obtained from semilogarithmic anamorphoses of the kinetic curves of CL decay in the first region are presented below ($[\mathrm{DPA}]_0 = 1 \cdot 10^{-6}$ mol g^{-1}).

T/°C	65	70	75	80
$k''_{\rm CL} \cdot 10^2/s^{-1}$	1.1	1	2.1	3.3

Like Ru^{II}, DPA catalyzes the decomposition of DMD. The effective activation parameters of the process obtained from the data presented are the following:

$$\log k''_{\rm CL} = (10.0 \pm 5.0) - (19.0 \pm 7.0)/\theta \ (r = 0.92),$$

where $\theta = 2.303RT$ kcal mol^{-1}.

The results obtained allow us to hope that oxidation of other surface-supported PAH by adsorbed DMD is also accompanied by CL. In this case, we can speak of a convenient method for studying the kinetics of these reactions. However, further experiments are required to verify this possibility.

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