CHEMICALLY INITIATED ELECTRON-EXCHANGE LUMINESCENCE OF $Ru(bpy)_3Cl_2$ IN CATALYTIC REACTION WITH 1,2-DIOXETANE

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We have investigated chemiluminescence activated by $Ru(bpy)_3Cl_2$ in the reaction of decomposition of 1,2-dioxetane. Catalysis and activation of chemiluminescence of 1,2-dioxetanes by a ruthenium complex occur according to a mechanism of chemically initiated electron exchange, which leads to effective excitation of $Ru(bpy)_3Cl_2$ with yield $\Phi^{*}_{Ru} = 0.20 \pm 0.05$.

Intermolecular reversible electron transfer in the reaction between a peroxide (dioxetane or dioxetanone) and an activator (fluorescent hydrocarbon) with low oxidation potential leads to efficient formation of a singlet-excited activator. This mechanism, called chemically initiated electron-exchange luminescence (CIEEL), ensures a high yield of the observed chemiluminescence (CL) of the peroxide [1, 2]. In order to enhance the intensity of chemiluminescence, in addition to organic activators it has also been suggested that complexes of f and d elements which luminesce well be used [3, 4]; the latter activate luminescence according to the traditional energy transfer mechanism, but in a number of cases catalyze the decomposition of peroxide [5]. It has been determined that the coordination-unsaturated complex $Eu(fod)_3$ enhances chemiluminescence and simultaneously accelerates decomposition of dioxetanes [5, 6] without changing the degree of oxidation of Eu. However, even for metal activators, electron-transfer reactions should play an important role in the mechanism of chemiluminescence. In [4], the catalytic process of intermolecular CIEEL has been suggsted as a possible route for enhancement of the chemiluminescence of dioxetanes by the $Ru(bpy)_3Cl_2$ complex.

This paper is devoted to evidence for the presence of CIEEL in decomposition of stable adamantyl-containing dioxetane in the presence of $Ru(bpy)_3Cl_2$.

EXPERIMENTAL

1,2-Dioxetane (I) (anti-isomer of endo,endo-2,3-dicarbo-methoxynorbornane-7-spiro-3-[1',2'-dioxetane]-4-spiro-2-adamantane) was obtained as described in [7]. $Ru(bpy)_3Cl_2$ was synthesized according to the technique in [8]. The solvent MeCN, purified by azeotropic distillation, has 70% transmittance at 200 nm. The chemiluminescence was recorded using the FÉU-140 photoelectron multiplier on an apparatus calibrated in absolute units according to the method in [9]. The spectral sensitivity of the photocathode was determined using a tungsten ribbon-filament lamp SIRSh-6-100 and a set of interference light filters in the region 365-670 nm. The sensitivity of the photocathode in the region of luminescence of Ru(II) was 5% relative to the maximum in the 410-450 nm region. The chemiluminescence (CL) and photoluminescence (PL) spectra were recorded on an apparatus fitted with a high-transmission SSR-1 monochromator and the FÉU-119 photoelectron multiplier. The activation parameters for chemiluminescence (E_a^{CL}) (I) in the presence of Ru(II) were determined from the temperature dependence of the intensity of chemiluminescence (50-70°C). The kinetic parameters for dark decomposition of (I) and in the presence of Ru(II) were measured at 113-137°C, using sealed ampuls, which were placed in a steel housing. After certain time intervals (0.75-1 h), the ampuls were removed, rapidly cooled down to a temperature of 75°C, the intensity of chemiluminescence (I_{75}) was measured, and then the procedure was repeated; I_{75} was proportional to the concentration of undecomposed (I). The quantum yield of photoluminescence of Ru(II) in air-saturated and degassed MeCN was determined using a quinine

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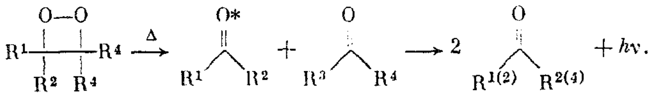
standard [10]. The excitation yields of ketones formed upon decomposition of (I) were determined by the chemiluminescent method, using selective acceptors for the excitation energy: 9,10-dibromoanthracene (for the triplets) and 9,10-diphenylanthracene (for the singlets). The errors in the yield measurements was <25%.

RESULTS AND DISCUSSION

Thermolysis of simple (alkyl-, aryl-, alkoxy-substituted) dioxetanes leads to decomposition into two carbonyl fragments, one of which with some probability is formed in the excited (preferentially triplet) state



(1)

In the presence of activators, the observed chemiluminescence upon thermolysis of dioxetanes is enhanced and is generally due to radiative deactivation of the activator. However, not only the chemiluminescence yield but also the rate of decomposition of dioxetanes can depend on the nature of the activator used.

Earlier the process of electronic excitation of Ru(II) upon activation of chemiluminescent thermolysis of adamantylideneadamantane-1,2-dioxetane (II) (the thermolysis product is adamantanone (III)) was considered drawing on the CIEEL mechanism [4]

$$\begin{aligned}&Ru(II) + (II) \overset{K}{\rightleftarrows} [Ru(II) \cdot + (II)] \xrightarrow{k_{ET}} [Ru(III) + (II)^{-}] \rightarrow [Ru(III) +\\ &+ (III)^{-} + (III)] \rightarrow [Ru^{*}(II) + (III) + (III)] \rightarrow Ru^{*}(II) +\\ &+ 2(III) \rightarrow Ru(II) + 2(III) + h\nu,\end{aligned} \qquad (2)$$

where K is the stability constant of the complex Ru(II) + (II); k_{ET} is the rate constant for electron transfer.

The observed rate constant for thermolysis of (II) in the presence of Ru(II) is described by the simple equation

$$k_{obs} = k_1 + k_2[Ru(II)], \qquad (3)$$

where k_1 is the rate constant for unimolecular decomposition of (II), k_2 is the bimolecular rate constant for the reaction.

Due to the small value of $k_2 \leq 10^{-3}$ liters/(mole·sec) (at 400 K), no effect of Ru(II) on dark decomposition of (II) was noted, even though the activation energy obtained from the temperature dependence of the intensity of chemiluminescence in the presence of Ru(II) was significantly lower than for chemiluminescent decomposition of (II). Based on the existing difference in activation energies and the absence of an appreciable contribution from luminescence of adamantanone (due to absorption of its radiation by the Ru(II) complex) to the total intensity of chemiluminescence, we hypothesized that chemiluminescence in the system Ru(II) + (II) reflects only the bimolecular activation branch of thermal decomposition of (II)

$$(II)-\left[\begin{array}{l}\xrightarrow{k_1} (III)^{*} + (III) \xrightarrow{Ru(II)} 2(III) \quad \text{No chemiluminescence}\\ \xrightarrow{k_2[Ru(II)]} Ru^{*}(II) + 2(III) \longrightarrow Ru(II) + 2(III) + h\nu.\end{array}\right. \qquad (4)$$

The rate of decomposition of (II) along the bimolecular branch of the process depends both on the ratio of the redox potentials of the pairs dioxetane/dioxetane radical anion and Ru(III)/Ru(II), and on the value of K, since $k_2 = K \cdot k_{ET}$. The oxidation potential of Ru(II) is equal to 1.28 V [11], which obviously also determines the small value of k_2 for (II). Assuming that (I) has more favorable values of $E_{(I)/(I^-)}$ and (or) K for occurrence of the bimolecular reaction than (II), we studied the chemiluminescence of (I) in the presence of Ru(II).

Thermolysis of (I) is accompanied by appreciable chemiluminescence. Its decomposition products are the ketones (III) and (IV)

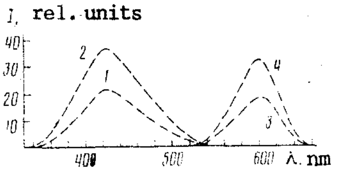


Fig. 1. Chemiluminescence spectra for thermolysis of 1) 10^{-2} (I); 2) 10^{-2} (II); 3) 5·10^{-3} (I) and 10^{-3} mole/liter $Ru(bpy)_3Cl_2$ in MeCN at 80°C; 4) photoluminescence spectrum of 10^{-3} mole/liter $Ru(bpy)_3Cl_2$ in MeCN (25°C, λ_{exc} = 436 nm).

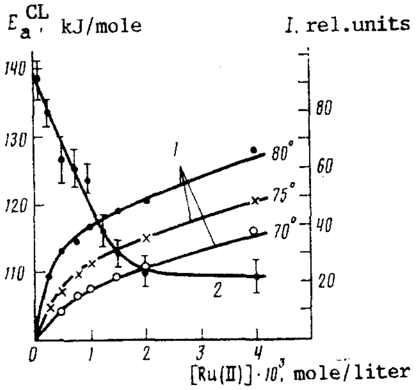


Fig. 2

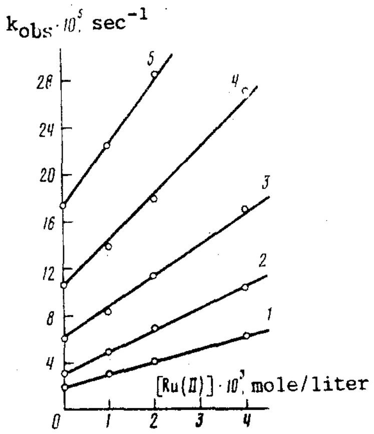
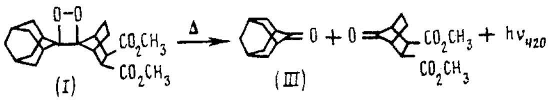


Fig. 3

Fig. 2. Dependence of the intensity of chemiluminescence (1) and the effective value E_a^{CL} of $Ru(bpy)_3Cl_2$ (2) upon decomposition of (I) on the concentration of $Ru(bpy)_3Cl_2$([I] = 10^{-3} mole/liter).

Fig. 3. Dependence of the observed rate constant for dark decomposition of (I) on the concentration of $Ru(bpy)_3Cl_2$ for different temperatures: 1) 390; 2) 395; 3) 400; 4) 405; 5) 410 K.



The chemiluminescence spectrum of (I) coincides with the chemiluminescence spectrum of (II) (Fig. 1), the emitter for which is (III). Possibly (III) is the emitter for the chemiluminescence of (I), but the ketones (III) and (IV) have close spectral characteristics, while the conditions under which the spectra are recorded (λ ∿ 10 nm) do not allow us to determine on which of the ketones the excitation is localized. The excitation yields in decomopsition of (I) are 0.5 and 8.5% for the singlet-excited and triplet-excited ketones respectively.

Upon addition of Ru(II) to a solution of (I), a change occurs in the spectral composition of the chemiluminescence. Since Ru(II) has a broad intense absorption band in the region of luminescence of (III) (log ε_m = 4.16), only emission of Ru(II) is apparent in the spectrum. The chemiluminescence and photoluminescence spectra of the system Ru(II) + (I), obtained under identical conditions, coincide (Fig. 1). With an increase in the Ru(II) concentration, the chemiluminescence flares (Fig. 2). When [Ru(II)] > 10^{-3} moles/liter, the dependence has a tendency toward saturation; but obviously this is not connected with the process of energy transfer from the excited ketone but more likely is due to concentration quenching of Ru*(II) and self-absorption of luminescence, since energy transfer, as was shown in [4], is not very efficient in activation of luminescence of dioxetanes by ruthenium.

Dioxetane (I) belongs to the class of stable compounds. We determined: $E_a = 141.3 + 6.3$ kJ/mole, $\log A = 14.0 \pm 1.0$ ($\Delta H^{\neq} = 139.2 \pm 6.3$ kJ/mole, $\Delta S^{\neq} = 3.1 \pm 2$ entropy units). The intensity of chemiluminescence of a solution of (I) containing $2 \cdot 10^{-3}$ mole/liter Ru(II) over the course of 2-3 h thermolysis at 80°C remains constant, which is evidence for little consumption of dioxetane and allows us to determine the activation energy for chemiluminescence (E_a^{CL}) for different activator concentrations. It turned out that E_a^{CL} (taking into account the activation energy for luminescence of Ru(II) E_a^{PL} – 27.6 kJ/mole) decreases with an increase in [Ru(II)] (Fig. 2) and reaches the limiting value of 109.5 kJ/mole for $4 \cdot 10^{-3}$ mole/liter. Probably the limiting value of E_a^{CL} corresponds to catalytic decomposition of (I) in the presence of Ru(II). If we assume that luminescence of Ru(II) upon thermolysis of (I) is due either to reemission of the luminescence of (III) or to transfer of the excitation energy from the ketone, then in this case E_a^{CL} will coincide with the activation energy for chemiluminescence upon thermolysis of (I), i.e., 138 ± 2.1 kJ/mole. Since E_a^{CL} for $0 <$ [Ru(II)] $> 1.5 \cdot 10^{-3}$ varies from 138 to 112.8 kJ/mole, probably the intermediate values of E_a^{CL} reflect a mixed process, with a contribution to the chemiluminescence both from uncatalyzed decomposition (obviously, reemission by ruthenium of the luminescence of the ketone), and from catalytic decomosition of (I) initiated by ruthenium. We determined the kinetic and activation parameters for dark decomposition of (I) in the presence of Ru(II) (Table 1), which allowed us to refine the mechanism for catalysis and activation of chemiluminscence.

The kinetics of dark decomopsition of (I) are characterized by the rate constant k_1. We found that in the presence of Ru(II), decomposition of (I) occurs according to first-order kinetics, but the observed rate constant for the reaction is proportional to the concentration of Ru(II) (Fig. 3). Thus in fact ruthenium catalyzes the decomposition of dioxetane, which is appreciable not only from the chemiluminescence. The slope of the straight lines obtained for different temperatures corresponds to the bimolecular rate constant k_2 of the reaction of Ru(II) with (I).

From the temperature dependence of k_2, given below (Table 2), we determined $E_a = 26.1 \pm 1.5$ and $\log A = 13.0 \pm 1.5$ for the bimolecular reaction

$$\mathrm{Ru(II)} + \mathrm{(I)} \xrightarrow{k_2} \mathrm{Ru(II)} + \mathrm{(III)} + \mathrm{(IV)} + h\nu. \tag{5}$$

From this it is obvious that the activation parameters obtained in a study of the chemiluminescence and dark decomposition of (I) coincide. Consequently, the chemiluminescence reflects only the catalytic route to decomposition of (I), the rate of which however is very small: at 70°C and for [Ru(II)] = $2 \cdot 10^{-3}$ mole/liter, $k_2 = 2.33 \cdot 10^{-4}$ liter/(mole·sec). But if we compare the estimate of the upper limit for the rate constant of catalytic decomposition of (II) with the rate constant for decomposition of (I), obviously in accordance with our assumptions (I) decomposes much faster than (II) (>200 times).

According to the presented mechanism, the intensity of activated chemiluminescence can be rewritten in the following form

$$I_{CL} = \Phi_{PL} \Phi_{Ru^*} k_2 [\mathrm{Ru(II)}] \cdot [\mathrm{(I)}], \tag{6}$$

where Φ_{PL} is the quantum yield of photoluminescence of Ru(II), Φ_{Ru}^* is the excitation yield of Ru(II). From Eq. (6) we can estimate the value of Φ_{Ru}^*. Thus at 70° $\Phi_{PL} = 1.1 \cdot 10^{-3}$, the intensity of chemiluminescence, taking into account the spectral sensitivity of the photoelectron multiplier $I_{PL} = 6.1 \cdot 10^7$ photons/sec for [Ru(II)] = $2 \cdot 10^{-3}$ mole/liter and the amount of (I) 0.001 mmole, $k_2 = 2.33 \cdot 10^{-4}$ liter/(mole·sec). From this the chemical excitation yield is $\Phi_{Ru}^* = 0.2 \pm 0.05$. The chemical excitation yield of Ru(II) in the reaction with (I) is comparable with the excitation yield in the reaction of Ru(III) with the hydrated electron, equal to 0.32 [12]. The total yield of excited ketones ($\Phi_T^* + \Phi_S^*$) upon thermolysis of (I) is 0.09, which is less than the yield of Ru*(II); consequently the value of Φ_{Ru}^* cannot be provided by transfer of excitation energy. The data obtained confirm the hypothesis in [4] concerning excitation of Ru(II) in catalytic reactions with simple dioxetanes according to the CIEEL mechanism, essentially involving the following. After initiating electron transfer from Ru(II) to (I) and rapid decomposition of dioxetane in the solvent

TABLE 1. Activation Parameters for Dark Thermal Decomposition of (I) in the Presence of Ru(II)

[Activator]$\cdot 10^{-3}$, mole/liter	Observed rate constant for decomposition of (I) $k_{obs}\cdot 10^5$, sec^{-1} (400 K)	E_a ±1,5, kJ/mole	lg A±1,0
–	6,37	141,3	14,0
1	8,39	132,9	13,3
2	11,3	125,8	12,8
4	16,9	127,9	13,0

TABLE 2. Values of the Bimolecular Rate Constant as a Function of Temperature

T, K	390	395	400	405	410
$k_2\cdot 10^2$, liters/(mole·sec)	1,10	1,82	2,60	3,92	5,31

cage, Ru(III) and the ketone radical anion are formed:

$$\mathrm{Ru(II)} + \mathrm{(I)} \overset{K}{\rightleftarrows} [\mathrm{Ru(II)} + \mathrm{(I)}] \xrightarrow{k_{ET}} [\mathrm{Ru(III)} + \mathrm{(I)}^-] \longrightarrow [\mathrm{Ru(III)} + \mathrm{(III)}^- + \mathrm{(IV)}] \quad (8)^{\dagger}$$

$$\begin{tikzcd}
{[\mathrm{Ru(III)} + \mathrm{(III)}^- + \mathrm{(IV)}]} \arrow[r, "\Phi^*_{Ru}"] \arrow[d, "1-\Phi^*_{Ru}"] & {[\mathrm{Ru^*(II)} + \mathrm{(III)} + \mathrm{(IV)}]} \arrow[r] & \mathrm{Ru^*(II)} + \mathrm{(III)} + \mathrm{(IV)} \arrow[d] \\
{[\mathrm{Ru(II} + \mathrm{(III)} + \mathrm{(IV)}]} \arrow[r] & \mathrm{Ru(II)} + \mathrm{(III)} + \mathrm{(IV)} & \mathrm{Ru(II)} + h\nu.
\end{tikzcd} \quad (9)$$

The electron is not clearly localized on either of the two ketones, (III) or (IV); there possibly exists a transition state in which both ketones participate [1]. The ketone radical anion formed is a strong reducing agent and its reaction with Ru(III) with efficiency Φ_{Ru}^* leads to excitation of Ru(II).

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† As in Russian original – Editor.