Excitation of chemiluminescence in the reaction of benzophenone-*O*-oxide with diphenyldiazomethane. Quantum-induced decomposition of diphenyldiazomethane

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The excitation yield (Ф*) of triplet benzophenone in the chemiluminescence reaction of thermal decomposition of diphenyldiazomethane (Ph_2CN_2) was measured. Triplet benzophenone was produced by the reaction of benzophenone-*O*-oxide with Ph_2CN_2 in a MeCN solution. The Ф* value is equal to 0.05 and temperature-independent. Analysis of the dependences of the observed rate constant of chemiluminescence decay on the concentration of Ph_2CN_2 both in the presence and absence of a luminescence activator suggests the quantum-induced decomposition of diazomethane in the reaction with triplet benzophenone. The rate constant of the reaction of triplet benzophenone with Ph_2CN_2 was estimated.

Key words: chemiluminescence, excitation yield, diphenyldiazomethane, carbonyl oxide.

Thermal decomposition of diazo compounds in the presence of O_2 is a convenient and promising method for the synthesis and study of highly reactive intermediates, carbonyl oxides.[1] It has previously been established that the thermal decomposition of diphenyldiazomethane (Ph_2CN_2) in the presence of dioxygen is accompanied by chemiluminescence (CL).[2] The kinetics of decomposition of Ph_2CN_2 has been studied, and the stage of chemiexcitation has been substantiated.[3] In this work, we determined the excitation yield in the reaction of carbonyl oxide with diphenyldiazomethane in acetonitrile and found evidence for the decomposition of Ph_2CN_2 quantum-induced by triplet benzophenone.

Experimental

Ph_2CN_2 was synthesized and purified according to the known procedure.[8] Chelate $Eu(TTA)_3Phen$ (TTA is thenoyltrifluoroacetylacetone, Phen is 1,10-phenanthroline) was synthesized according to the procedure presented previously.[9] Acetonitrile (special-purity grade) was dried with P_2O_5 and distilled. The CL intensity was measured on a photometric installation supplied with an FEU-140 photoamplifier. CL spectra were recorded on an MZD-2M wide-aperture monochromator using an FEU-119 photoamplifier. Photoluminescence spectra were recorded on an MPF-4 Hitachi spectrofluorimeter. The spectral sensitivity of the photocathode of an FEU-140 photoamplifier was determined with an SIRSh-6-100 ribbon tungsten lamp and a set of interference light filters in the spectral region of 365—670 nm. The viscosity of acetonitrile was determined on an Ubellohde viscosimeter.

Results and Discussion

Based on our previous results[3] and known published data,[4–7] we propose the following scheme of thermal decomposition of Ph_2CN_2, formation of carbonyl oxide, and chemiluminescence in an oxygen-containing solution.

Scheme 1

$$Ph_2CN_2 \xrightarrow[k_0]{} {}^1Ph_2C: + N_2, \qquad (0)$$

$$^1Ph_2C: \rightleftharpoons {}^3Ph_2C:, \qquad (ST, TS)$$
$$k_{ST} = 3.2 \cdot 10^9$$
$$k_{TS} = 6.3 \cdot 10^6$$

$$^1Ph_2C: + Ph_2CN_2 \longrightarrow Ph_2C{=}N{-}N{=}CPh_2, \qquad (1.1)$$
$$k_1 = 2.3 \cdot 10^{10}$$

$$^3Ph_2C: + Ph_2CN_2 \longrightarrow Ph_2C{=}N{-}N{=}CPh_2, \qquad (2.1)$$
$$k_{21} = 3.4 \cdot 10^7$$

$$^3Ph_2C: + O_2 \longrightarrow Ph_2C^{\cdot}OO^{\cdot}, \qquad (2.2)$$
$$k_{22} = 5 \cdot 10^9$$

$$Ph_2C^{\cdot}OO^{\cdot} + Ph_2CN_2 \longrightarrow {}^3Ph_2C{=}O^* + Ph_2C{=}O + N_2, \qquad (3.1)$$
Ф* — excitation yield

$$Ph_2C^{\cdot}OO^{\cdot} + Ph_2C^{\cdot}OO^{\cdot} \longrightarrow 2\,Ph_2C{=}O + O_2, \qquad (3.2)$$
$$2k_{32} = 3 \cdot 10^7$$

$$^3Ph_2C{=}O^* \longrightarrow Ph_2C{=}O + h\nu, \qquad (4.0)$$
Φ_P, τ_p — phosphorescence yield and lifetime

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$$^3Ph_2C{=}O^* + Ph_2CN_2 \longrightarrow Ph_2C{=}O + Ph_2CN_2 \qquad (4.1)$$

$$\longrightarrow {}^3Ph_2C\colon + Ph_2C{=}O + N_2,$$

$$^3Ph_2C{=}O^* + O_2 \longrightarrow Ph_2C{=}O + {}^1O_2,\ O_2, \qquad (4.2)$$

$$k_{42} = 3 \cdot 10^9$$

$$^1O_2 \longrightarrow O_2, \qquad (5.0)$$

$$k_{50} \approx 2 \cdot 10^4$$

$$^1O_2 + Ph_2CN_2 \longrightarrow Ph_2COO + N_2. \qquad (5.1)$$

$$k_{51} = 1 \cdot 10^9$$

Based on analysis of the composition of the products, the kinetics of decomposition of Ph_2CN_2 studied by spectrophotometry, and comparison with the data of chemiluminescence measurements, we conclude that benzophenone is excited in reaction (3.1). The enthalpy of this reaction ($\Delta H = -124$ kcal mol^{-1})[3] is enough for the formation of $Ph_2C{=}O$ in the triplet excited state. The CL excitation is considered as the transition of the reacting system from the ground state to the excited state *via* the reaction route from the starting reagents to the products.[10] The excitation yield is the probability of conversion of the chemical energy into energy of electron excitation and is an important magnitude that characterizes a chemiluminescence reaction. Under stationary conditions, the intensity of observed CL is determined by the equation

$$I_{CL} = \Phi_P\Phi^*w, \qquad (1)$$

where Φ_P is the phosphorescence yield of benzophenone, Φ^* is the excitation yield, and w is the reaction rate.

The excitation yield can be determined if the phosphorescence yield of ketone $\Phi_P = k_p\tau_0$ is known from independent experiments. However, this value is very low and strongly affected by admixtures; therefore, it is difficult to measure it under the conditions (composition of the solution, temperature, viscosity) in which CL is studied. Another approach is more convenient and reliable: the transfer of excitation energy to the luminophore, which plays the role of an amplifier (activator) of CL. $Eu(TTA)_3Phen$ is the most appropriate compound as such an activator.[11] CL increases during thermolysis of Ph_2CN_2 in the presence of $Eu(TTA)_3Phen$, and the spectral composition of luminescence changes (Fig. 1). The spectrum of activated CL coincides with the photoluminescence spectrum of the Eu^{III} chelate and corresponds to the transitions $^5D_0 \rightarrow {}^7F_j$. Since ^3BP is the emitter of nonactivated CL, the triplet-triplet energy transfer to the ligand of the europium complex followed by the intramolecular energy transfer to the excited levels of the central ion is the most probable mechanism of population of excited levels of the activator.

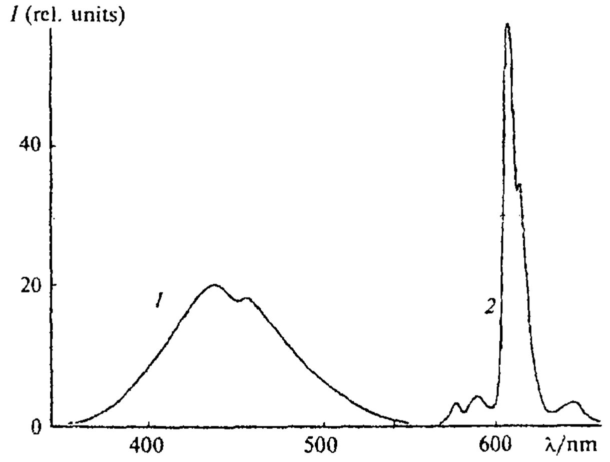


Fig. 1. CL spectrum during thermolysis of $5 \cdot 10^{-4}$ mol L^{-1} Ph_2CN_2 (*1*) and in the presence of $5 \cdot 10^{-4}$ mol L^{-1} $Eu(TTA)_3Phen$ (*2*) in MeCN at 343 K.

In the presence of the activator, Scheme 1 should be supplemented by reactions of excitation energy transfer to the luminophore and luminescence

$$^3Ph_2C{=}O^* + Eu(TTA)_3Phen \xrightarrow{k_{et},\ \Phi_{et}}$$

$$\longrightarrow Ph_2C{=}O + Eu^*(TTA)_3Phen,$$

$$Eu^*(TTA)_3Phen \xrightarrow{\Phi_A} Eu(TTA)_3Phen + h\nu.$$

The intensity of activated CL is the following:

$$I_{CL,Eu} = \Phi_A\Phi_{et}\Phi^*w, \qquad (2)$$

where Φ_A is the quantum yield of photoluminescence of $Eu(TTA)_3Phen$, $\Phi_{et} = k_{et}\tau_p[A]$ is the yield of energy

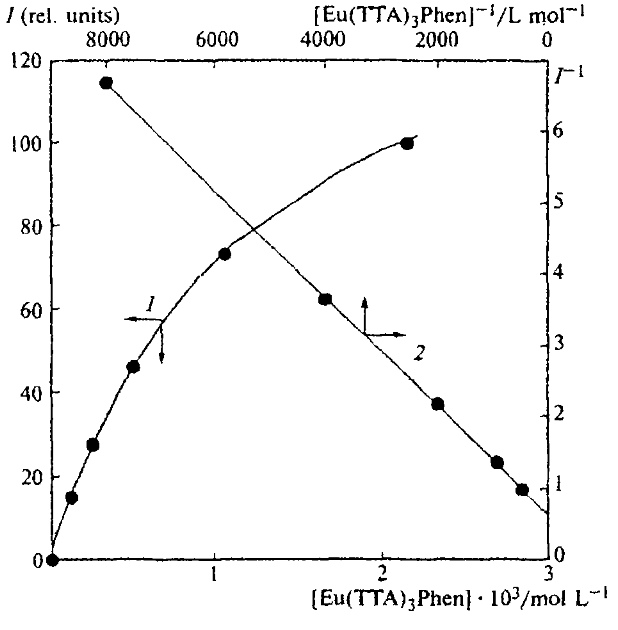


Fig. 2. Dependence of the CL intensity during thermolysis of $5 \cdot 10^{-4}$ mol L^{-1} Ph_2CN_2 on the concentration of $Eu(TTA)_3Phen$ at 343 K (*1*) and linear anamorphosis of curve *1* (*2*) in the coordinates of Eq. (3).

Table 1. Stern constants (k_{et}), real lifetimes of benzophenone (τ_p), CL decay rate constants (k_{CL}), quantum yields of CL (Φ_{CL}), photoluminescence of the activator (Φ_A), and excitation in acetonitrile (Φ^*) in the decomposition of Ph_2CN_2

T/K	$k_{et}\tau_p{}^0$ /L mol^{-1}	$\tau_p{}^0 \cdot 10^{-8}$ /s	$k_{CL} \cdot 10^{-4}$ /s^{-1}	$I_{CL,Eu}{}^{III} \cdot 10^{-9}$ /photon s^{-1} mL^{-1}	$\Phi_{CL,Eu}$	Φ_A	Φ^*
328	790	6.1	0.46	8.6	0.24	0.20	0.047
333	800	5.7	0.80	19.2	0.34	0.16	0.055
338	803	5.3	1.40	38.4	0.40	0.13	0.052
343	810	5.1	2.40	63.0	0.49	0.10	0.049

Note. The CL decay rate constant and the absolute intensity were determined with an accuracy of ±10—14%; the Stern constant, quantum yields of CL, and excitation were determined with an accuracy of ±20—30%.

transfer, k_{et} is the diffusion-limited rate constant of energy transfer, $\tau_p = \tau_p{}^0(1 + k_{et}\tau_p{}^0[A])^{-1}$ is the lifetime of triplet benzophenone in the presence of A, and $\tau_p{}^0$ is the same in the absence of A.[12]

The excitation yield is determined from the limited (at $\Phi_{et} = 1$, *i.e.*, at $[A] = \infty$) intensity of activated CL, the segment cut on the ordinate axis of the linear dependence $I_{CL,Eu}{}^{-1}$—$[Eu^{III}]^{-1}$:

$$1/I_{CL,Eu} = 1/\Phi_A\Phi^* w\{1 + [1/(k_{et}\tau_p{}^0[A])]\}. \qquad (3)$$

To calculate the excitation yield, one should know the photoluminescence yield of $Eu(TTA)_3Phen$ in a certain solvent at a specified temperature and the reaction rate. The influence of the solvent and temperature on the quantum yield of photoluminescence of $Eu(TTA)_3Phen$ has previously been studied in detail.[3] It is seen in Fig. 2, which demonstrates the dependence of the CL intensity on the concentration of the Eu^{III} chelate, that Eq. (3) is well fulfilled. The Stern constant $k_{et}\tau_p{}^0$ was found from the segment cut on the ordinate axis and the tangent slope (Table 1). The rate constant of energy transfer is diffusion-limited and amounts to $k_{et} = k_{diff} = 8RT(3000\eta)^{-1} = 1.3 \cdot 10^{10}$ L mol^{-1} s^{-1} at 328 K and $1.6 \cdot 10^{10}$ L mol^{-1} s^{-1} at 343 K. The real lifetime of benzophenone was calculated from the obtained Stern constants and k_{diff} (see Table 1).

Taking into account Scheme 1, the CL intensity in the absence of the activator is determined by the following equation:

$$I_{CL} = \Phi_P\Phi^*\{k_p/(k_p + k_{41}[Ph_2CN_2] + k_{42}[O_2])\} \times \\ \times k_0[Ph_2CN_2], \qquad (4)$$

where $k_p = (\tau_p{}^0)^{-1}$ is the rate constant of deactivation of ^{3}BP obtained from Eq. (3), Φ_P is the quantum yield of phosphorescence of BP, and k_0 is the decay rate constant of Ph_2CN_2.

In Eq. (4), the value $\alpha = k_p(k_p + k_{41}[Ph_2CN_2] + k_{42}[O_2])^{-1}$ is the coefficient that takes into account the quenching of triplet benzophenone in reactions (4.1) and (4.2). Under our experimental conditions, $k_p = 2 \cdot 10^7$ s^{-1} at 70 °C, $[Ph_2CN_2] \le 5 \cdot 10^{-4}$, and $[O_2] = 7 \cdot 10^{-4}$ mol L^{-1} = const, from which it follows that $k_p > k_{41}[Ph_2CN_2]$ and $k_p > k_{42}[O_2]$ even in the case when k_{41} is diffusion-limited. Due to this, the quasi-stationary CL intensity is proportional to the concentration of Ph_2CN_2 within the range of changing its concentration from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ mol L^{-1} (Fig. 3). Taking this into account, we obtain the equation

$$I_{CL} \approx \Phi_P\Phi^* k_0[Ph_2CN_2], \qquad (5)$$

which is valid only at $[Ph_2CN_2] < 5 \cdot 10^{-4}$ mol L^{-1}.

The decay rate constant of Ph_2CN_2 (k_0) was calculated from the overall rate constant of the decomposition of Ph_2CN_2 measured from the rate of CL decay[3]:

$$k_0 = 0.5k_{CL}. \qquad (6)$$

The k_{CL} values, the intensity of activated CL, the quantum yield of CL, and the excitation yield calculated

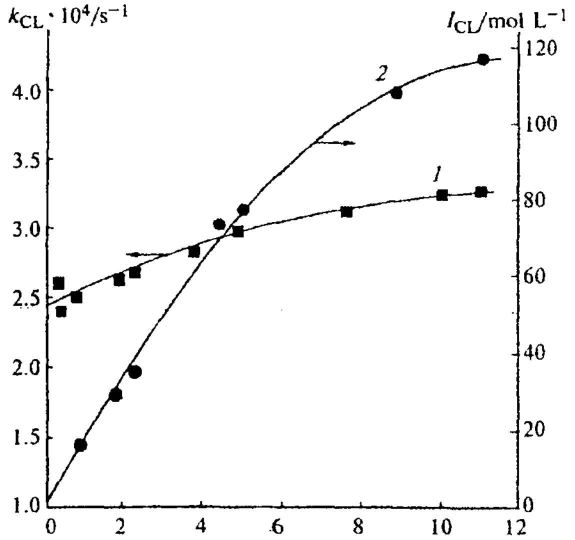


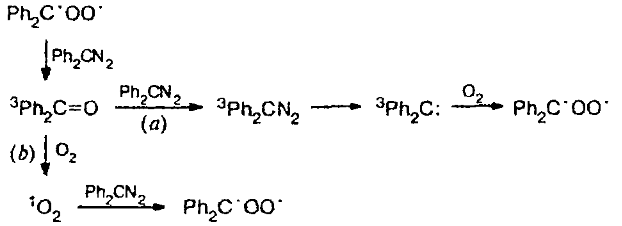
Fig. 3. Dependences of the observed rate constant of CL decay (*1*) and CL intensity (*2*) on the concentration of Ph_2CN_2 at 343 K in MeCN.

from Eq. (3) are presented in Table 1. It is seen that the Φ^* value is sufficiently high and close to that of thermal decomposition of 1,2-dioxetanes,[14] which does not rule out the participation of triplet benzophenone in the quantum-induced decomposition of diphenyldiazomethane (reactions (4.1) and (5.1)).

The role of reactions (2.1), (4.1), and (5.1) increases as the concentration of Ph_2CN_2 increases. This should result in an increase in the observed rate constant of CL decay and a negative deviation from the linear dependence of I_{CL} on $[Ph_2CN_2]$. In fact, these changes in k_{CL} and I_{CL} are experimentally observed (see Fig. 3).

The excitation energy transfer from ^3BP to Ph_2CN_2 results most likely in its decomposition in reaction (4.1) and further in the participation of the carbene formed in successive stages of chain reaction (Scheme 2, route *a*).

Scheme 2



The relatively high excitation yield of BP makes this process highly probable.

The quenching of ^3BP with dioxygen to form its singlet state with the rate constant close to the diffusional value is another possibility that explains the dependences of k_{CL} and I_{CL}. The yield of $^1O_2$ in this reaction amounts to 0.29[15] and, hence, the participation of singlet oxygen in the induced decomposition of Ph_2CN_2 is also highly probable (see Scheme 2, route *b*). The participation of ^3BP in the quantum-induced decomposition of Ph_2CN_2 can be established if a quenching agent is introduced into the system. For example, the increase in the reduced relative CL intensity in the dependence of absence and presence of the Eu^{III} chelate on the Ph_2CN_2 concentration (see Fig. 3) is the result of the quenching of ^3BP with the chelate and its absence from the reactions presented in Scheme 2.

The fraction of quantum-induced decomposition of Ph_2CN_2 can be estimated from the equation[3]

$$k_{CL}^{obs} = 2k_0(1 - \Phi)^{-1}, \qquad (7)$$

where

$$\Phi = \Phi^*(\Phi_{41}k_{41}[Ph_2CN_2] + \Phi_{42}k_{42}[O_2])\times \\ \times(k_{41}[Ph_2CN_2] + k_{42}[O_2])^{-1}, \qquad (8)$$

where Φ_{41} is the quantum yield of formation of Ph_2C: in reaction (4.1), and Φ_{42} is the quantum yield of $^1O_2$ in reaction (4.2). The estimated fraction of the quantum-induced decomposition of Ph_2CN_2 in Eq. (8) is ~5% at $[O_2] = 7 \cdot 10^{-4}$ mol L^{-1} and $[Ph_2CN_2] = 10^{-3}$ mol L^{-1} in the first cycle of the chain process.

In experiments, the fraction of the quantum-induced decomposition of Ph_2CN_2 is determined as the ratio

$$\Phi = (k_{CL}^{obs} - 2k_0)(k_{CL}^{obs})^{-1}, \qquad (9)$$

where k_{CL}^{obs} is the observed rate constant of CL decay during the quantum-induced decomposition of Ph_2CN_2. At an initial concentration of Ph_2CN_2 of 10^{-4} mol L^{-1}, reactions (4.1) and (5.1) can be neglected; therefore, $k_{CL}^{obs} = 2k_0$. At $[Ph_2CN_2] = 10^{-3}$ mol L^{-1}, $k_{CL}^{obs} > 2k_0$; thus, the fraction of the quantum-induced decomposition of Ph_2CN_2 calculated from Eq. (9) is 14±7%.

The divergence in estimations is associated with the possible ignoring of other routes of induced decomposition of diphenyldiazomethane, in particular, in reactions (1.1) and (2.1), and with the fact that the chain length >1.

Another evidence in favor of the quantum-induced decomposition of Ph_2CN_2 is the influence of the activator on the dependence of the CL intensity on the concentration of Ph_2CN_2. For example, the presence of the activator results in the quenching of benzophenone and, hence, its absence from the chain process.

In the presence of 10^{-3} mol L^{-1} $Eu(TTA)_3Phen$, the conditions $k_{et}[Eu^{III}] > k_{41}[Ph_2CN_2]$ and $k_{et}[Eu^{III}] > k_{42}[O_2]$ are fulfilled. The ratio of intensities of nonactivated and activated CL is determined by the following correlation:

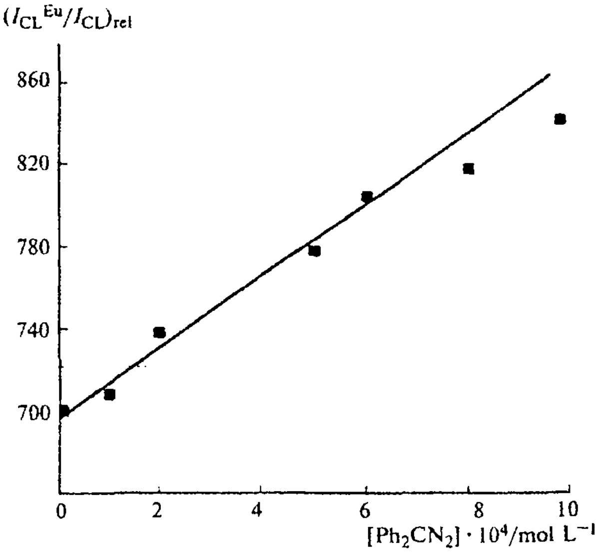


Fig. 4. Dependences of the ratio of CL intensities in the presence of 10^{-3} mol L^{-1} $Eu(TTA)_3Phen$ and in the absence of the activator on the concentration of Ph_2CN_2 at 343 K in MeCN.

$$I_{CL}/I_{CL,Eu} = \{\Phi_P(k_p + k_{41}[Ph_2CN_2] + k_{42}[O_2] + k_{et}[Eu^{III}])\}/\{\Phi_A(k_p + k_{41}[Ph_2CN_2] + k_{42}[O_2])\}. \quad (10)$$

Equation (9) can easily be transformed:

$$I_{CL,Eu}/I_{CL} = (k_p + k_{42}[O_2])/k_{et}[Eu^{III}] + (\Phi_P k_{41}/\Phi_A k_{et}[Eu^{III}]) \cdot [Ph_2CN_2]. \quad (11)$$

The correlation $\Phi_P k_{41}(\Phi_A k_{et}[Eu^{III}])^{-1}$, equal to $1.8 \cdot 10^{-5}$ at $[Eu^{III}] = 10^{-3}$ mol L^{-1} and 70 °C, was determined from relation (10) (Fig. 4). Taking into account that $k_{et}[Eu^{III}] \approx 1.2 \cdot 10^7$ s^{-1}, $\Phi_P = 10^{-5}$,[12] and $\Phi_A = 0.1$, we obtain $k_{41} \approx 2 \cdot 10^8$ L mol^{-1} s^{-1}. Thus, the rate constant of reaction (4.1) is ~600 times lower than the diffusional rate constant, and one-two of a hundred collisions of ^3BP with Ph_2CN_2 result in the quenching of benzophenone, whose mechanism is most likely chemical, *i.e.*, results in the decomposition of Ph_2CN_2.

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