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Chemiluminescence during thermolysis of the $(Ph_3COOCPh_3)_n$—$Ph_3C^{\cdot}$ peroxide containing captured triphenylmethyl radical*

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Chemiluminescence (CL) in the thermolysis of $(Ph_3COOCPh_3)_n$—$Ph_3C^{\cdot}$ containing the triphenylmethyl radical captured during the synthesis of Gomberg's peroxide was found. Two CL emitters were identified: the triplet state of benzophenone ($^3Ph_2CO^*$) and $Ph_3C^{\cdot *}$. $Ph_3C^{\cdot *}$ is formed due to the energy transfer from the excited $^3Ph_2CO^*$ generated in the disproportion of thermolysis intermediates, $Ph_3CO^{\cdot}$ radicals. This $Ph_3C^{\cdot *}$ luminescence is the first example of CL activation by an organic radical. Chemiluminescence during the thermolysis of $Ph_3COOCPh_3$ containing no $Ph_3C^{\cdot}$ is resulted from the emission of one emitter, $^3Ph_2CO^*$. The solid-phase CL was found during the oxidation of $Ph_3C^{\cdot}$ with dioxygen after the destruction of the crystalline lattice as a result of the thermolysis of the $(Ph_3COOCPh_3)_n$—$Ph_3C^{\cdot}$ peroxide.

Key words: chemiluminescence, photoluminescence, triphenylmethyl radical, di(triphenylmethyl) peroxide, thermolysis of peroxides, activation of chemiluminescence.

Thermolysis of several organic peroxides is accompanied by chemiluminescence (CL), whose emitters are ketones in a triplet state.[1] In the presence of activators, organic molecules or luminescent metal complexes,[2] CL is enhanced due to energy transfer from the primarily excited emitters to activators or *via* the mechanism of chemically initiated electron-exchange luminescence.[2—4] In this work, we studied the thermolysis of the peroxide $(Ph_3COOCPh_3)_n$—$Ph_3C^{\cdot}$ (**1**) containing the captured $Ph_3C^{\cdot}$ radical and showed for the first time that the organic $Ph_3C^{\cdot}$ radical can act as the CL activator.

Experimental

A sample of Ph_3CCl (purity grade) was three times recrystallized from hexane. Toluene and hexane (reagent grade) were dried by standard procedures.[5] Argon was purified from H_2O and O_2 according to a previously described procedure.[6] Peroxides were synthesized by the oxidation with O_2 of a solution of $Ph_3C^{\cdot}$ obtained by the known[7] reaction of Ph_3CCl with zinc powder. The $Ph_3C^{\cdot}$ radical was identified in a solution before its oxidation by the ESR spectra and photoluminescence (PL). $Ph_3COOCPh_3$ (**2**) containing no $Ph_3C^{\cdot}$ was synthesized by a continuous O_2 feed to a solution of Ph_3CCl (0.18 mmol) in toluene (298 K) followed by the addition of Zn (1.56 mmol). Precipitate **2** that formed was recrystallized similarly to a procedure described previously.[8] To synthesize peroxide **1** containing $Ph_3C^{\cdot}$, we performed the reaction of Ph_3CCl (0.18 mmol) in toluene (298 K) with Zn (1.56 mmol) under argon. A solution containing $Ph_3C^{\cdot}$ and its dimer was separated from Zn by centrifuging, after which the reactor with the solution was connected to a burette with O_2. Oxidation was carried out until O_2 absorption ceased and $Ph_3C^{\cdot}$ and the dimer were completely consumed. The precipitate of **1** was washed with anhydrous toluene. Compounds **1** and **2** were characterized by elemental analysis data, PL and ESR spectra, and melting temperatures. The amount of the $Ph_3C^{\cdot}$ radical in sample **1** was determined by the ESR method relatively to the standard (the Mn^{2+} sample produced at the VNIIFTRI). The thermolysis of **1** and **2** (0.048 mmol) was carried out in a quartz CL cell in an argon atmosphere with the temperature control by a thermocouple. The activation energy (E_a) of the thermolysis of **1** was determined from the stepped plot of the CL intensity *vs.* temperature.[9] The thermolysis products, Ph_2CO and Ph_3COPh, were identified by the phosphorescence (PS) and IR spectra and mass spectrometry.

PL and ESR spectra were recorded on an Aminco-Bowman fluorimeter and an SE/X-2542 Radiopan spectrometer. CL spectra were measured on a setup described previously.[6] IR spectra (KBr) were measured on a Specord IR-75 spectrophotometer, and mass spectra were recorded an MI-1201V mass spectrometer.

Results and Discussion

The PL spectrum of the obtained solution of $Ph_3C^{\cdot}$ (λ_{max}/nm: 525, 550) coincides with the PL spectra of solutions of $Ph_3C^{\cdot}$ in toluene and THF recorded for the first time[10,11] at 300 K. When these $Ph_3C^{\cdot}$ solutions are frozen to 77 or 90 K, a short-wave shift in the PL spectra (λ_{max}/nm: 518, 545) is observed,[11—14] as well as

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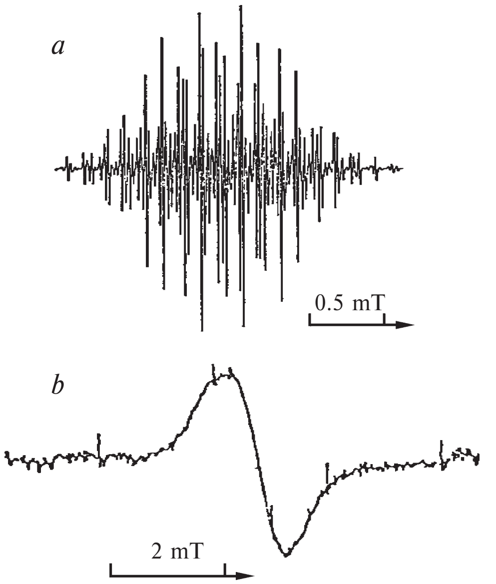


Fig. 1. ESR spectra of the $Ph_3C^{\cdot}$ radical (298 K): *a*, solution in toluene (10^{-4} mol L^{-1}); and *b*, solid sample of **1**.

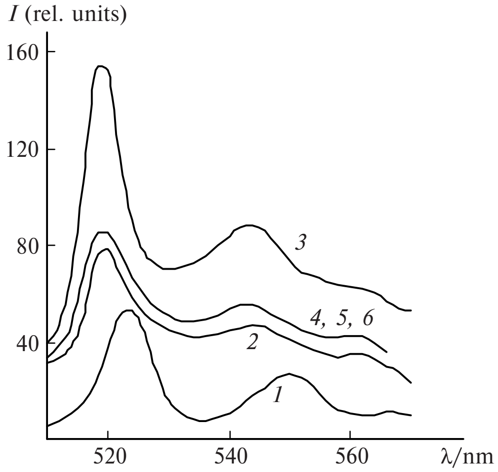


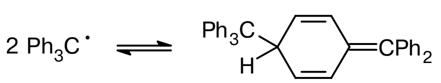
Fig. 2. PL spectra of the $Ph_3C^{\cdot}$ radical: *1*, solution of $Ph_3C^{\cdot}$ obtained by the reaction of Ph_3CCl (0.18 mmol) with Zn (1.56 mmol) in toluene (300 K); *2* and *3*, suspension of peroxides in a solution immediately after precipitation; *4*, *5*, and *6*, solid samples of **1** after the action of toluene, saturated H_2O (1 h), and air (1 h) and boiling in toluene (1 h). Temperature of PL detection: 298 (*1*, *2*, *4*, *5*, *6*) and 77 K (*3*).

in the PL spectra of the $Ph_3C^{\cdot}$ radical prepared by the photolysis[15] or radiolysis[16] of solutions of Ph_3CCl or Ph_3CH vitrified at 77 K.

The ESR spectrum of a solution of $Ph_3C^{\cdot}$ in toluene (Fig. 1, *a*) is a well resolved multiplet with the HFC constants $a_{o\text{-H}}(6\ H) = 0.255$ mT, $a_{p\text{-H}}(3\ H) = 0.278$ mT, and $a_{m\text{-H}}(6\ H) = 0.111$ mT, which agree with published values.[17] Radical **1** has characteristics typical[8] of Gomberg's peroxide, m.p. 458—459 K. Found (%): C, 87.7; H, 6.20; O, 6.10. $C_{38}H_{30}O_2$. Calculated (%): C, 88.0; H, 6.17; O, 5.83. IR, ν/cm^{-1}: 975 and 758 (O—O). However, unlike compound **2**, sample **1** at 298 K exhibits an intense green PL and an ESR signal, which is characteristic of $Ph_3C^{\cdot}$. The ESR spectrum (Fig. 1, *b*) represents a singlet line with $\Delta H_{1/2} \approx 1.1$ mT and $g = 2.0027$. The estimations of the number of radicals captured by the crystalline lattice show that 1 g of sample **1** contains $4.8 \cdot 10^{17}$ $Ph_3C^{\cdot}$ or one radical per 1000 peroxide molecules. The PL spectra of compound **1** (λ_{max}/nm: 518, 545) measured at 77 and 298 K are identical (Fig. 2) and coincide with the PL spectra of solutions of $Ph_3C^{\cdot}$ frozen at 77 K in which the radical exists in the crystalline matrices.

The $Ph_3C^{\cdot}$ radical captured by the peroxide is more stable than that in a solution. For example, when O_2 is fed to a solution containing $Ph_3C^{\cdot}$ and its dimer, 5—10 min after (depending on the concentration of $Ph_3C^{\cdot}$ and dimer) the PL and ESR signal from the radical disappear completely. At the same time, the PL and ESR spectra remain unchanged upon prolonged (>1.5 years) storage of compound **1** in air or in toluene saturated with H_2O (see Fig. 2). Heating of **1** in boiling toluene (1 h) under Ar does not either result in a decrease in the PL brightness and escape of $Ph_3C^{\cdot}$ to a solution (see Fig. 2). The contact of compound **1** (or its suspension in toluene at 353 K) with O_2 does not result in CL usually observed[10] for the autooxidation of $Ph_3C^{\cdot}$ in a solution, which confirms the stabilization of $Ph_3C^{\cdot}$ in the peroxide matrix. It is most likely that the high stability of $Ph_3C^{\cdot}$ is related to lower diffusion coefficients of dioxygen and water in the crystalline sample of **1** compared to those in solutions of $Ph_3C^{\cdot}$.

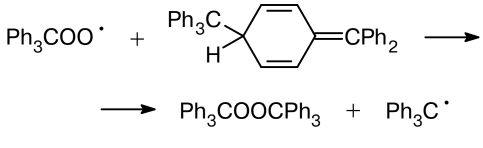
The stability of $Ph_3C^{\cdot}$ could be a consequence of the adsorption of these radicals on the solid peroxide surface. To check this possibility, we prepared separately a solution of $Ph_3C^{\cdot}$ and solid sample **2**. Then these components were thoroughly mixed and stored for 2 h under argon, after which the solid phase was separated by centrifuging. It turned out that the reaction product exhibits neither PL nor ESR signal. Thus, the stabilization of $Ph_3C^{\cdot}$ occurs, most likely, during the formation of the peroxide crystalline lattice. To explain the effect of $Ph_3C^{\cdot}$ stabilization, we propose the following hypothesis. As known,[7] $Ph_3C^{\cdot}$ in a solution exists in an equilibrium with molecular dimer.



(1)

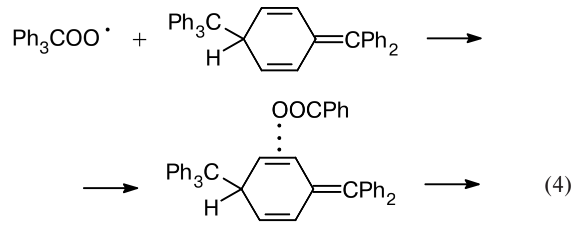
Among main[7] reactions of peroxide formation by radical autooxidation (reactions (2) and (3)), reaction (3) is of the most interest because the components of compound **1** simultaneously form precisely in this reaction.

$$Ph_3COO^{\cdot} + Ph_3C^{\cdot} \longrightarrow Ph_3COOCPh_3 \qquad (2)$$



(3)

Taking into account the capability of peroxide radicals of forming π-complexes with aromatic compounds,[18,19] we can suggest that reaction (3) includes stages of the formation and decomposition of this π-complex.



(4)

$$\longrightarrow Ph_3COOCPh_3 + Ph_3C^{\bullet} + (Ph_3COOCPh_3)_{n-1} \quad (5)$$

$$\longrightarrow (Ph_3COOCPh_3)_n\text{—}Ph_3C^{\bullet} \quad (6)$$

Most these complexes are decomposed in reaction (5) to form **2** and $Ph_3C^{\bullet}$, which remains in a solution and then participates in the chain radical autooxidation of the dimer. However, a minor portion of the π-complexes is involved into the crystallization of the peroxide (reaction (6)) to afford compound **1**.

On heating sample **1** in an Ar atmosphere to the melting point (459 K), CL appeared (I(m.p.) = $5.4 \cdot 10^6$ photon s^{-1} mL^{-1}). After thermolysis at temperatures higher than m.p. and a 80% decrease in the CL intensity compound **1** was cooled (393 K) to the complete luminescence decay. Then an O_2 flow was fed to the cell filled with the solidified sample, and a new CL appeared due to the autooxidation of $Ph_3C^{\bullet}$. Therefore, the thermal decomposition of **1** results in a release of the captured $Ph_3C^{\bullet}$ and its oxidation with O_2, which is accompanied by CL. Note that this luminescence is the first example of CL detection during the oxidation of an organic radical in the solid phase.

Among the thermolysis products we identified benzophenone by its characteristic[20] PL (Fig. 3) and absorption band in the IR spectra at 1665 cm^{-1} and $PhOCPh_3$ by the mass spectrum (EI, 70 eV), m/z (I_{rel} (%)): 336 $[M]^+$ (33), 259 $[M - Ph]^+$ (100), 182 $[M - 2\ Ph]^+$ (14), 166 $[M - 2\ Ph - O]^+$ (21). The same products were previously[21] found in the study of the dark thermolysis of sample **2**.

Since the luminescence intensity is weak, the CL spectrum measured during the thermolysis of **1** (503 K) using a set of boundary light filters is arranged in the region of 400—600 nm (see Fig. 3). The short-wave region of the CL spectrum, the PL spectrum (77 K) of the thermolyzed sample **1**, and the PL spectrum (77 K) of benzophenone are arranged in the same region of 400—500 nm, *i.e.*, the triplet state of benzophenone $^3Ph_2CO^*$ is a CL emitter during the thermolysis of **1**. The long-wave component of the CL spectrum (500—600 nm), which makes a great contribution to the emission, lies in the PL region of the radical and is resulted from the emission of $Ph_3C^{\bullet *}$. The CL intensity during the thermolysis of sample **2** (I(m.p.) = $5.1 \cdot 10^6$ photon s^{-1} mL^{-1}) containing no $Ph_3C^{\bullet}$ is somewhat lower than the CL intensity during the thermolysis of **1**, and the CL spectrum (503 K) is presented by the emission of only one emitter, $^3Ph_2CO^*$ (see Fig. 3).

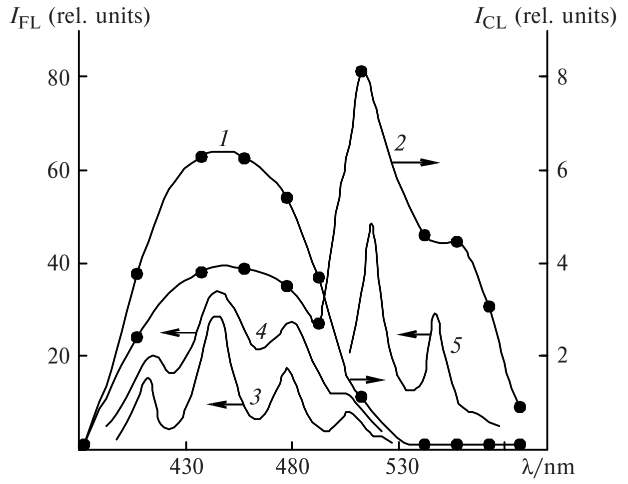


Fig. 3. Luminescence spectra during thermolysis of peroxides: chemiluminescence of samples **2** (*1*), **1** (*2*), PL of Ph_2CO at λ_{exc} = 313 nm (*3*); FL before (*4*) and after thermolysis of compound **1** (*5*) at λ_{exc} = 340 nm. Temperatures of detection: 473 (*1*, *2*), 77 (*3*, *5*), and 298 K (*4*).

The activation energy (E_a) of the thermodecomposition of compound **1** determined from the temperature plot of the CL intensity (Fig. 4) is 27±2 kcal mol^{-1}. It is known[22] that the O—O bond strength (E_{O-O}) for different symmetric dialkyl peroxides is almost the same and equals 38 kcal mol^{-1}. A decrease in E_a for $Ph_3COOCPh_3$ can be resulted from the destabilization of the peroxide due to the steric repulsion of the bulky phenyl substituents. The thermochemical estimation of the E_{O-O} value for **2** gives 30 kcal mol^{-1}, which agrees with the experimental E_a value. In calculations, ΔH_f° = 70 kcal mol^{-1} for the $Ph_3CO^{\bullet}$ radical was taken from published data,[23] and ΔH_f° = 110 kcal mol^{-1} for $Ph_3COOCPh_3$ was calculated by the method of additivity of thermochemical increments.[24]

$$E_{O-O} = 2\Delta H_f^{\circ}(Ph_3CO^{\bullet}) - \Delta H_f^{\circ}(Ph_3COOCPh_3) = \\ = 2 \cdot 70 - 110 = 30\ (\text{kcal mol}^{-1})$$

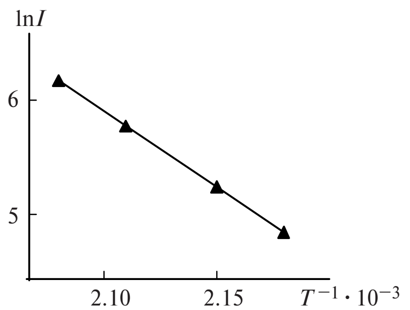


Fig 4. Plot of the logarithm of the CL intensity (ln$I$) *vs.* temperature during thermolysis of compound **1**.

Based on the experimental results and published data on CL during the thermolysis of other peroxides,[1,25] we can propose the mechanism of CL appearance during the thermolysis of **1** (Scheme 1).

Scheme 1

$$Ph_3COOCPh_3)_n\text{—}Ph_3C^{\cdot} \longrightarrow [(Ph_3COOCPh_3)_{n-1} + (Ph_3CO^{\cdot}...{}^{\cdot}OCPh_3)...Ph_3C^{\cdot}] \longrightarrow$$

$$\rightarrow [(Ph_3COOCPh_3)_{n-1}, PhOCPh_3, Ph_2C{=}O^*, Ph_3C^{\cdot}] \rightarrow$$

$$\rightarrow (Ph_3COOCPh_3)_{n-1}, PhOCPh_3, Ph_2C{=}O, Ph_3C^{\cdot} + h\nu\ (400\text{—}500\ \text{nm})$$

$$\rightarrow [(Ph_3COCPh_3)_{n-1}, PhOCPh_3, Ph_2C{=}O, Ph_3C^{\cdot}*] \rightarrow$$

$$\longrightarrow (Ph_3COOCPh_3)_{n-1}, PhOCPh_3, Ph_2C{=}O, Ph_3C^{\cdot} + h\nu\ (500\text{—}600\ \text{nm})$$

It is known[25] that the disproportionation of the tertiary oxyl radicals $R_3CO^{\cdot}$ in solutions occurs according to the reaction

$$R_3CO^{\cdot} + R_3CO^{\cdot} \longrightarrow R_3COR + R_2CO, \qquad (7)$$

and, as shown,[25] excited ketones can also be formed. In the peroxide melt, due to a lower mobility than that in a solution, the probability of this reaction is likely higher than that of the reaction of $R_3CO^{\cdot}$ with other participants of the process. The calculation of the thermal effect ($\Delta H°$) of the disproportional of the $Ph_3CO^{\cdot}$ radicals (see Scheme 1) using previously published data[23,26] gives the value

$$\Delta H° = \Delta H_f°(Ph_3COPh) + \Delta H_f°(Ph_2CO) - 2\Delta H_f°(Ph_3CO^{\cdot}) = 52.1 + 12 - 2\cdot 70 = -75.9\ (\text{kcal mol}^{-1}).$$

This value agrees well with the results in Ref. 1, according to which the thermal effects of $R_3CO^{\cdot}$ disproportionation for the phenyl and alkyl derivatives, including cyclic derivatives, differ slightly and range within 75—82 kcal mol^{-1}. Thus, the energy reserve of the disproportionation of the $Ph_3CO^{\cdot}$ radicals is sufficient for the population of the triplet level of benzophenone (72 kcal mol^{-1}). The radiative deactivation of $^3Ph_2CO^*$ results in phosphorescence in the region of 400—500 nm (see Scheme 1). It is most likely that $Ph_3C^{\cdot}$ is excited due to the energy transfer to $Ph_3C^{\cdot}$. The energy transfer to an acceptor decreases the luminescence intensity of a donor[2] and, as can be seen in Fig. 3, the intensity of the benzophenone component of the CL spectrum during the thermolysis of **1** is lower than that for **2**.

Chemiluminescence during the thermolysis of **1** is the first example of the activation of chemical reaction luminescence due to the energy transfer from an excited organic molecule to a free radical.

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