

# Chemiluminescence Accompanying the Decomposition of Dibenzoyl Peroxide in Pyridine

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In this paper the chemiluminescence accompanying the thermal decomposition of dibenzoyl peroxide in pyridine has been studied. It has been found that the temporal course of the intensity of chemiluminescence corresponds to the rate of dibenzoyl peroxide decomposition and that it is possible to base on this phenomenon a method for kinetic study of the above reaction.

The kinetics of the reaction of amines with peroxides involving chemiluminescence was hitherto investigated mainly by *Vasiljev* and *Nalbandan* [1, 2]. For instance, these authors correlated the reactions of 10 aromatic amines (dimethylaniline and its derivatives, diphenylamine, and some derivatives of oxazole) with dicyclohexyl percarbonate. The temporal course of the intensity of radiation was different in individual reactions. Some differences were also observed in the spectral composition of emitted light, in the effect of reagents, and even in the kinetics of the reaction involving chemiluminescence.

The chemiluminescence radiation appearing during the decomposition of dibenzoyl peroxide in pyridine was mentioned for the first time by *Whitehouse* and *Jennings* in their recent paper [3].

The sufficiently high values of the intensity of chemiluminescence radiation produced by this system stimulated us to investigate the possibility of using the chemiluminescence method for kinetic study. The aim of this paper is to compare the curves of the chemiluminescence intensity decrease with the kinetic curves of the decrease in dibenzoyl peroxide concentration determined iodometrically. On the basis of the identification of the reaction products the mechanism of the chemiluminescence rise as well as the kind of radiation emitter are discussed. Some characteristics of this radiation especially the lifetime and the chemiluminescence spectrum were determined.

## Experimental

Dibenzoyl peroxide was purified by a twofold precipitation from a chloroform solution with methanol and subsequently dried *in vacuo* at 1 Torr (m.p. 104°C). Pyridine anal. grade was dried with barium oxide and distilled.

For the determination of dibenzoyl peroxide the following procedure proved to be convenient: 20 ml of ice-cold acetic acid was put into 5 ml of the pyridine solution containing dibenzoyl peroxide (0.1–0.2 mol l<sup>-1</sup>), then the solution was bubbled through with nitrogen for 5 minutes and mixed with 10 ml of potassium iodide solution in ice-cold acetic acid. Subsequently the solution was bubbled through with nitrogen again and kept for 1/2 hour in the dark. Then the solution was diluted with 15 ml of distilled water and, after adding starch jelly, titrated with 0.05 N-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

The measurements of chemiluminescence were performed with a photometric instrument PU SNK 7M, developed at the Institute of Chemical Physics of the Academy of Sciences of USSR in Moscow, which was equipped with a photomultiplier FEU-38 (photocathode SbNaKC<sub>2</sub>). To measure the chemiluminescence spectrum, the interference filters were put one after the other before the cathode of photomultiplier. The intensity values were then corrected for individual filters in intervals of 10–15 nm with respect to the sensitivity of photocathode and the transmittance of filters.

The intensity of chemiluminescence is given in the so-called relative units. The arbitrary unit corresponds thus to the current of  $3.6 \times 10^{-13}$  A when the resistance of circuit is  $1 \times 10^{11} \Omega$ .

The separation of the reaction products formed during the decomposition of dibenzoyl peroxide in pyridine was carried out by gel permeation chromatography. A glass column, having the diameter of 28 mm and the height of gel layer of 790 mm, contained 125 g of Sephadex LH-20; methanol was used as a solvent.

The infrared spectra were recorded with a Unicam SP 200 spectrophotometer.

### Results and Discussion

The plots of the chemiluminescence intensity against time for the decomposition of dibenzoyl peroxide in pyridine and in an inert atmosphere at temperatures ranging from 55 to 105°C show a maximum (Fig. 1). This maximum is caused both by the heating of samples to the temperature of measurement and by the proper process of chemiluminescence. Provided pyridine is used as a solvent, the rate of the decrease in dibenzoyl peroxide concentration may be expressed by the equation

$$-\frac{d[\text{BP}]}{dt} = k[\text{BP}]. \quad (1)$$

This equation corresponds to a pseudounimolecular equation, where  $k = k_P[\text{P}]$  and the symbols [BP], [P], and  $k_P$  denote concentration of dibenzoyl peroxide, concentration of pyridine, and rate constant of a bimolecular reaction, respectively.

The intensity of chemiluminescence, which is proportional to the rate of formation of the excited particles and to the rate of dibenzoyl peroxide decomposition, thus obeys the equation

$$I = \eta_{\text{chem.}} [\text{BP}]_0 e^{-kt}, \quad (2)$$

where  $\eta_{\text{chem.}}$  is the quantum yield of chemiluminescence.

The time necessary to attain the maximum intensity (Fig. 1) does not practically differ from the time of heating of a sample to the temperature of measurement. That is why we used only the decreasing parts of the plots of the chemiluminescence intensity against time to evaluate our results. The shape of these plots as well as the values of maximum intensity  $I_{\text{max}}$  are functions of the temperature at which peroxide decomposition takes place. In contrast to the investigation of *Whitehouse and Jennings* [3], we did not observe any induction period, *i.e.* a shift of  $I_{\text{max}}$  to longer time intervals.

From the dependence of intensity logarithms on time which is linear ( $y$ -intercept equals  $\eta_{\text{chem.}} [\text{BP}]_0$  while the slope gives  $k$ ) the constants  $k_P$  were determined (Table 1). The activation energy of dibenzoyl peroxide decomposition in pyridine may be determined by using the relationship between the logarithm of the constant  $k_P$  and the reciprocal value of absolute temperature (Fig. 2). The activation energy thus determined and the

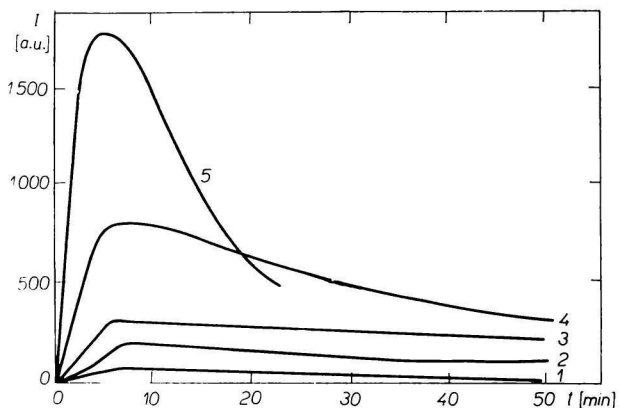


Fig. 1. Chemiluminescence intensity as a function of time for the decomposition of dibenzoyl peroxide in pyridine.

Initial concentration of peroxide  $0.2 \text{ mol l}^{-1}$ .

Temperature of decomposition: 1.  $54.0^\circ\text{C}$ ; 2.  $63.5^\circ\text{C}$ ; 3.  $71.0^\circ\text{C}$ ; 4.  $79.5^\circ\text{C}$ ; 5.  $91.5^\circ\text{C}$ .

Table 1

Rate constants of the bimolecular interaction between dibenzoyl peroxide and pyridine  $k_P$  and the values of maximum chemiluminescence intensity  $I_{\text{max}}$

$t$ [ $^\circ\text{C}$ ]	$1/T \times 10^3$ [ $\text{K}^{-1}$ ]	$k_P$ [ $\text{l mol}^{-1} \text{ s}^{-1}$ ]	$I_{\text{max}}$ [a. u.]
54.0	3.058	$6.35 \times 10^{-5}$	63
63.5	2.972	$9.47 \times 10^{-5}$	195
71.0	2.902	$1.52 \times 10^{-4}$	320
79.5	2.835	$4.22 \times 10^{-4}$	563
91.5	2.743	$9.46 \times 10^{-4}$	1800
104.0	2.652	$2.65 \times 10^{-3}$	5320

frequency factor enable us to express the rate constant of the interaction of benzoyl peroxide with pyridine in the form

$$k_P = 6.4 \times 10^7 \exp\left(\frac{18\,700 \pm 700}{RT}\right). \quad (3)$$

The relationship between the temporal course of chemiluminescence intensity and the kinetics of the decomposition of dibenzoyl peroxide in pyridine may also be illustrated by the measurements, in which another independent method is used to determine the decrease in peroxide concentration. The iodometric titration (Fig. 3) has shown that the decrease in dibenzoyl peroxide concentration and the temporal course of chemiluminescence intensity are identical in the investigated concentration region. (Intensity is given in %, i.e.  $I/I_{\text{max}} \cdot 100$ .) A similar agreement is obtained by comparing the chemilu-

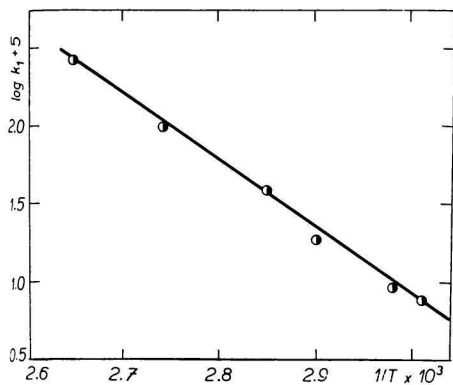


Fig. 2. Dependence of the logarithm of rate constants  $k_p$  on the reciprocal values of absolute temperature.

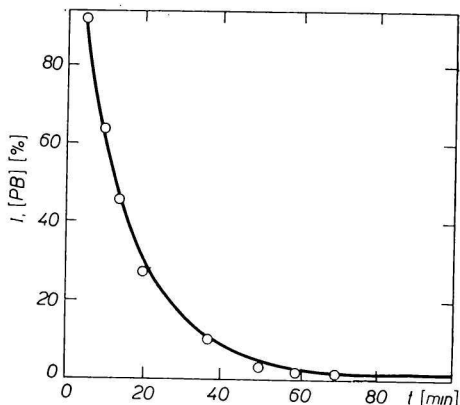


Fig. 3. Comparison between the chemiluminescence intensity during the decomposition of dibenzoyl peroxide in pyridine at  $90^\circ\text{C}$  and the content of dibenzoyl peroxide determined by iodometric titration.

— the course of intensity expressed in % of  $I_{\text{max}}$ ;  $\circ$  the content of dibenzoyl peroxide in sample  $[BP]_t/[BP]_0 \times 100$ .

minescence intensity with the transmittance values of the absorption band of carbonyl group ( $1780\text{ cm}^{-1}$ ).

To identify the radiation emitter in the chemiluminescence reaction under investigation, it was necessary to know the qualitative composition of the reaction products. On the basis of the knowledge of their luminescence properties as well as of the comparison of the literary data of excitation energy with the energy values corresponding to the

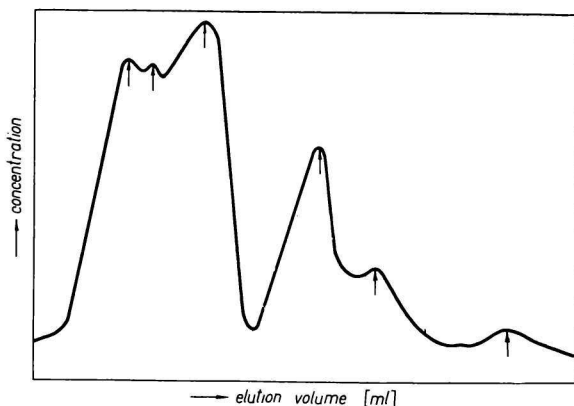


Fig. 4. Elution curve for the separation of the decomposition products of dibenzoyl peroxide in pyridine.

maximum in chemiluminescence spectrum, it is possible to determine by elimination method which of the reaction products is formed in electron excited state.

For the separation of the reaction products the gel permeation chromatography was used. As seen in Fig. 4, a great number of compounds were formed. After separating and concentrating successively the individual components,  $\alpha$  and  $\gamma$  phenylpyridine, benzoin

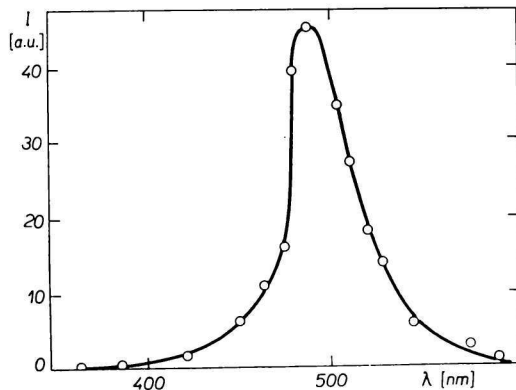


Fig. 5. Chemiluminescence spectrum for the decomposition of dibenzoyl peroxide in pyridine at 80°C.

acid, and pyridine-*N*-oxide were identified by usual analytical methods (infrared spectrophotometry, determination of melting point, *etc.*). The results obtained by analytical methods indicated that both pyridylbenzoic acid and phenylpyridylbenzene were present in the system. According to the above-mentioned criteria and the analysis of reaction products the radiating substance may be either phenylpyridylbenzene or phenylpyridine.

The chemiluminescence spectrum (Fig. 5) has a single emission band between 420 and 570 nm with a maximum at 495 nm. Therefore it seems that only one kind of excited particles is formed in the course of reaction. Other important characteristics of chemiluminescence reaction are the quantum yield and the lifetime of excited particle.

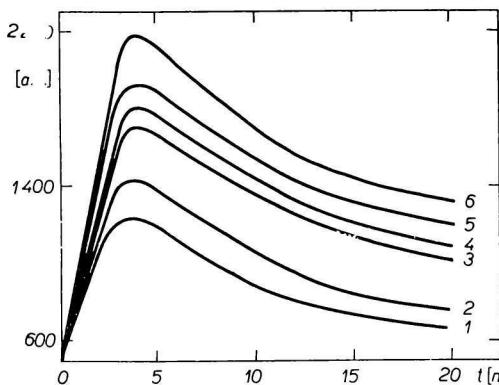
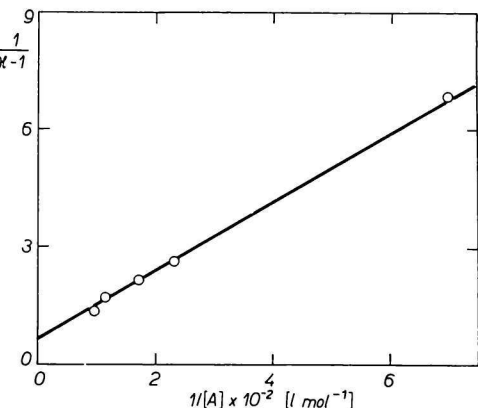


Fig. 6a. The temporal course of chemiluminescence intensity for the decomposition of benzoyl peroxide in pyridine with varying concentration of activator at 80°C.

1. without activator; 2. concentration of activator  $1.42 \times 10^{-3}$  mol l<sup>-1</sup>; 3. concentration of activator  $4.35 \times 10^{-3}$  mol l<sup>-1</sup>; 4. concentration of activator  $5.70 \times 10^{-3}$  mol l<sup>-1</sup>; 5. concentration of activator  $8.57 \times 10^{-3}$  mol l<sup>-1</sup>; 6. concentration of activator  $1.00 \times 10^{-2}$  mol l<sup>-1</sup>.

Fig. 6b. Dependence of the ratio  $1/\kappa - 1$  on the reciprocal value of the activator 9,10-dibromoanthracene concentration.



The quantum yield of radiation was determined by the method of activated chemiluminescence. The dibromo derivative of anthracene substituted in position 9,10 was used as an activator. The magnification coefficient of the chemiluminescence intensity due to activator  $\kappa$ , which is the intensity ratio in the presence of activator ( $I$ ) and without that ( $I_0$ ) is a linear function of concentration of 9,10-dibromoanthracene [4] (Fig. 6a, b) and satisfies the following relationship

$$\frac{1}{\kappa - 1} = \frac{\eta_X}{\eta_A - \eta_X} + \frac{1}{\eta_A - \eta_X} \cdot \frac{\eta_A}{K_{XA} \tau_X} \cdot \frac{1}{[A]}, \quad (4)$$

where  $\eta_X$ ,  $\eta_A$ ,  $K_{XA}$ , and  $\tau_X$  are the quantum yield of excited particles, the quantum yield of activator emission, the constant of energy transfer, and the lifetime of the excited state, respectively.

The extrapolation of the above relationship to  $1/[A] \rightarrow 0$  gives the ratio  $\eta_X/\eta_A - \eta_X$ . The quantum yield of activator radiation [4] has then the value  $\eta_A = 0.095$  photons for one excited molecule,  $\eta_X$  being  $3.7 \times 10^{-12}$  photon per one excited molecule. Provided the value of quantum yield with respect to the radiation of excited reaction product  $\eta_X$  is known, it is possible to determine the lifetime of the excited particle. The constant of energy transfer  $K_{XA}$  approximately equals the diffusion constant the value of which in solutions is  $10^9 - 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ . Then the value of  $\tau_A$  is  $10^{-8} - 10^{-7} \text{ s}$ .

Table 2

Some kinetic parameters for the decomposition of BP in benzene and pyridine

Parameter	System	
	BP in benzene	BP in pyridine
rate constant at 80°C	$4.6 \times 10^{-5} \text{ s}^{-1}$	$4.2 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$
activation energy of chemiluminescence process	30 kcal mol <sup>-1</sup>	18 kcal mol <sup>-1</sup>
quantum yield of radiation (photons per excited molecule)	$1 \times 10^{-4}$	$3.7 \times 10^{-2}$

The estimated lifetime of radiating particle as well as the fact that chemiluminescence is not quenched by oxygen gives evidence that the excited particle in the measured system is in an excited singlet state.

On the basis of these results it may be concluded that the radiation emission in the system dibenzoyl peroxide—pyridine arises in a bimolecular interaction of both relevant components. The high enough values of chemiluminescence intensity as well as the good reproducibility enables to investigate the proper kinetics of dibenzoyl peroxide decomposition. For comparison we present some characteristics of this chemiluminescence reaction in benzene [5] and pyridine (Table 2).

The chemiluminescence method proved to be very convenient for kinetic studies because the measurement of the intensity as a function of time enables to estimate rapidly and easily the instantaneous concentration of dibenzoyl peroxide and the rate constant of its decomposition without any quantitative analysis of the reaction system. The error of this method is smaller than 5%.

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