

A contribution to the kinetics of benzoyl peroxide decomposition in naphthalene

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The kinetic studies of benzoyl peroxide decomposition in naphthalene at temperatures ranging from 55 to 103°C have shown that this reaction is a chain process with an induced decomposition of first order. The chain propagation of this radical process is due to the interaction of solvent radical with peroxide while its termination is caused by a mutual deactivation of primary and secondary radicals. The temperature dependence of the rate constant of the overall decomposition reaction remains fluent even if the melting point of naphthalene is passed.

The decomposition of benzoyl peroxide in both aliphatic and aromatic hydrocarbons is generally considered to be a chain process with an induced decomposition of higher order [1] the propagation as well as the termination of which is due to radicals of the medium [2]. However, the composition of the products of this decomposition reaction [3] of which phenylnaphthalene, *i.e.* the product of the interaction between radical from peroxide and naphthalene is important, does not obey the above-mentioned rule.

In order to examine the mechanism of the benzoyl peroxide decomposition in naphthalene, we analyzed in this paper the kinetics of this process in the temperature range from 55 to 103°C. Since the melting point of naphthalene occurs in the temperature region where the decrease in benzoyl peroxide concentration was measured, this investigation offers a good opportunity to evaluate the effect of the phase change of medium on the character of decomposition reaction.

Experimental

Benzoyl peroxide was purified by threefold precipitation of its chloroform solution with methanol. The purity of the product determined iodometrically reached 99.8%.

Naphthalene used as decomposition medium for benzoyl peroxide was of anal. grade with m.p. 80.1°C.

Stilbene functioning as an inhibitor of the chain decomposition of peroxide was purified by zone melting; its. m.p. (123.7°C) being consistent with the tabulated value (124°C) [4].

The samples of naphthalene containing benzoyl peroxide or stilbene used for determination of the loss of peroxide at temperatures over the melting point of naphthalene were prepared by weighing individual components into glass test tubes which were sealed after tenfold repeated evacuation and refilling with nitrogen. Peroxide was mixed with stilbene in test tubes kept at the temperature of the thermostat. If the reaction kinetics was investigated below the melting point of naphthalene, the experiments were performed in a similar way, the only difference being that the test tubes used were

equipped with a side tube where peroxide or stilbene was placed during the melting of naphthalene in sealed test tubes. In this case the respective samples were prepared so that after the melting of naphthalene at 81.0°C the content of the side tube was quantitatively transferred into the test tube, dissolved under constant stirring for a short time, and the solution thus obtained was cooled to the temperature of thermostat. The reaction was carried out in an oil bath thermostat at ten temperatures ranging from 55 to 103°C.

After the completion of decomposition reaction the remaining peroxide was estimated by titration of iodine (with 0.01 N solution of sodium thiosulfate) released in slightly acid medium (caused by an addition of dry ice which simultaneously displaced air oxygen) from potassium iodide at laboratory temperature [5].

Results and discussion

It ensues explicitly from the results concerning the loss of benzoyl peroxide thus determined (Figs. 1 and 2) that a linear relationship exists between the concentrations of peroxide at the beginning and after the reaction which characterizes the unimolecular kinetics of the decomposition reaction independently of its course either in liquid or in solid naphthalene. At first sight it may seem to be a purely homolytic dissociation of peroxide without any contribution of the induced decomposition. But such a simplified idea does not agree with the results of experiments on the inhibition of the decomposition reaction (Fig. 3). Retardation of the peroxide decomposition in the presence of stilbene as well as the unimolecularity of the inhibited or non-inhibited decomposition leads to the conclusion that benzoyl peroxide decomposes by a chain reaction in naphthalene, too, but in contrast to other known cases the induced decomposition appears kinetically as a reaction of first order (independently of the state of aggregation of naphthalene).

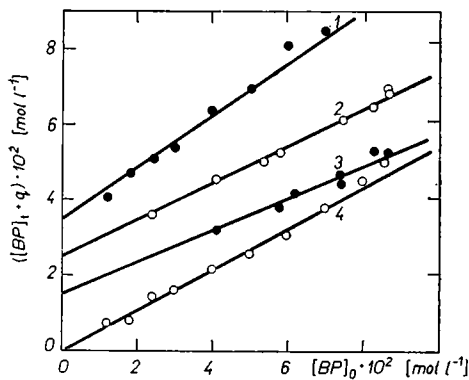


Fig. 1. Concentration of benzoyl peroxide after its decomposition in solid naphthalene ($[BP]_t$) as a function of the initial concentration ($[BP]_0$).

1. 55.0°C, 80 hrs ($q = 0.035$); 2. 68.0°C, 24 hrs ($q = 0.025$); 3. 76.0°C, 12 hrs ($q = 0.015$); 4. 79.5°C, 5 hrs ($q = 0$).

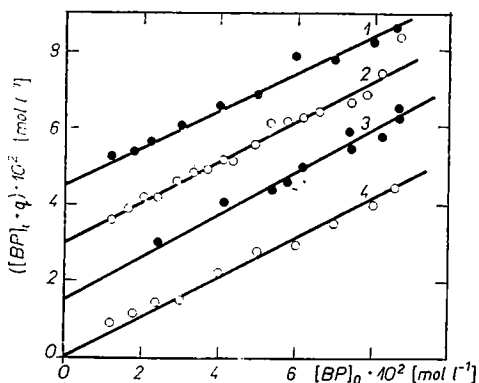


Fig. 2. Concentration of benzoyl peroxide after its decomposition in liquid naphthalene ($[BP]_t$) as a function of the initial concentration ($[BP]_0$).

1. 80.5°C, 5 hrs ($q = 0.045$); 2. 82.5°C, 3 hrs ($q = 0.030$); 3. 90.0°C, 1½ hrs ($q = 0.015$); 4. 103.0°C, 1½ hrs ($q = 0$).

Such relatively rare chain decomposition of first order involves some complications as regards the determination of the kinetic parameters of the decomposition process. First of all, because of the equality of the reaction orders it is not possible to express the rate constants of spontaneous (k_s) and induced (k_i) decomposition by usual

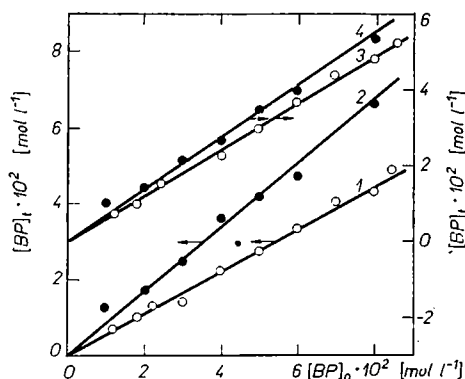


Fig. 3. Benzoyl peroxide decomposition in naphthalene.

1 and 2 below m.p. of naphthalene (60.5°C); 3 and 4 above its m.p. of naphthalene (98.0°C); 2 and 4 in the presence of stilbene; 1 and 3 in its absence. (Stilbene and peroxide were present in equimolar ratio.)

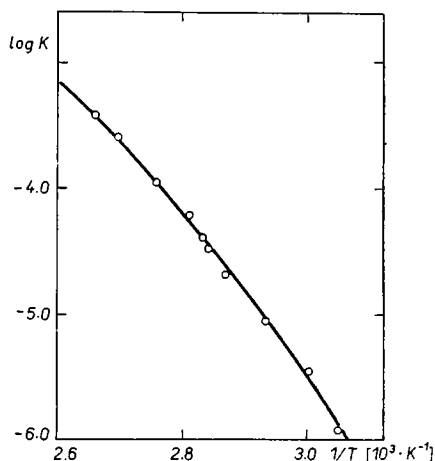


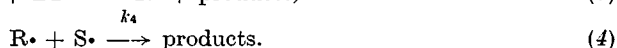
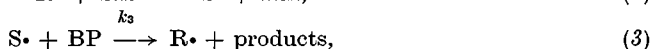
Fig. 4. Logarithm of the rate constant of the overall decomposition of benzoyl peroxide in naphthalene as a function of reciprocal absolute temperature.

kinetic analysis [6]. Since the inhibitory effect of stilbene is not quantitative either, the portion of spontaneous and induced decomposition may be only assessed. As a matter of fact, there are available a number of data on the rate constant of the spontaneous decomposition of this peroxide in different media at 80°C. These data vary predominantly in the range from 2×10^{-5} to $8 \times 10^{-5} \text{ s}^{-1}$ while most values for nonpolar medium (benzene, *tert*-butylbenzene, toluene) are near to $3.3 \times 10^{-5} \text{ s}^{-1}$ [1]. With respect to the rate constant of the overall decomposition of peroxide at 80.5°C determined in our experiments ($3.9 \times 10^{-5} \text{ s}^{-1}$), the probable portion of induced decomposition at this temperature is equal approximately to 15%, but it is not excluded that this portion may reach even higher values up to the maximum value of 50%.

It is worth noticing in this connection that the Arrhenius equation is not able to express the temperature dependence of the rate constant of the non-inhibited peroxide decomposition although it is a reaction of first order. The simple reason for this fact is that the rate constant represented in our case by the sum $k_s + k_i$ cannot be expressed by means of the usual exponential relation with corresponding activation energies differing in values. The deviation from linearity of the Arrhenius equation

thus inadequately used (Fig. 4) also demonstrates that the rate constant is not a rate constant of an elementary reaction but the sum of two above-mentioned terms. (The values of rate constants in Fig. 4 were calculated from the plots presented in Figs. 1–3 by using the common kinetic relationship for unimolecular reactions.)

The following sequence of elementary processes corresponds to the established unimolecular kinetics of the investigated decomposition reaction of benzoyl peroxide (BP) in naphthalene (SH)



Therefore phenylnaphthalene occurring among the products of decomposition may arise in process (4) either by direct recombination of phenyl (decarboxylation product of primary benzoyloxy radical $\text{R}\cdot$) and naphthyl radical $\text{S}\cdot$ or by disproportionation of phenylnaphthyl (secondary addition product [3]) and benzoyloxy radical. On the basis of the above scheme of peroxide decomposition the following kinetic relationship [6] may be deduced

$$\frac{-d[\text{BP}]}{dt} = k_s[\text{BP}] + \frac{k_2 k_3[\text{SH}]}{k_4} [\text{BP}]. \quad (5)$$

This equation involves an induced decomposition of first order, the rate constant of which equals the fraction

$$k_i = \frac{k_2 k_3[\text{SH}]}{k_4}.$$

The results of these investigations reveal another important fact, *i.e.* the continuity of the temperature dependence of the rate constant of the overall reaction even if the melting point of naphthalene is passed (80.1°C). It is very interesting that even such a marked change in the viscosity of decomposition medium which is produced by the change in the state of aggregation does not cause any appreciable deflection in the character of the relationship between rate constant and temperature. This deflection could be expected in principle because of a more significant increase in the cage recombination of primary radical pairs [7] in solid naphthalene.

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