The Catalytic Action of Organic Peroxides on the Polymerization of Ethenoid Compounds. III. The Effects of α-and β-Naphthoyl Peroxide on the Polymerization of Styrene

By Matsuji TAKEBAYASHI, Tadao SHINGAKI and Hisashi MATSUI

(Received May 25, 1954)

The reaction of free radicals in polymerization systems has been widely studied in particular as to the ability of a free radical to initiate and terminate reaction chains.[1] In the previous paper of this series,[2] the authors, studying the polymerization of styrene and of vinyl acetate in the presence of substituted benzoyl peroxides, observed that the activity of a radical derived from a peroxide was related to the distribution of electron density: thus electron repelling substituents increased the activity of a radical, and electron attracting substituents lowered the reactivity, and that the rate of polymerization was in a parallel relation with the rate of decomposition of peroxides, which generated active free radicals.

Recently, it has been found that some amines promote the decomposition of peroxides,[3] and that the peroxide-catalyzed polymerization of styrene is accelerated by adding tertiary amines[4] or polyamines.[5]

The experiments recorded in this paper have been carried out to investigate the effects of α-and β-naphthoyl peroxide on the polymerization of styrene and the influences of some tertiary amines on the effects of naphthoyl peroxides.

First of all, the rate of decomposition of the peroxide (1/6000 mol.) in styrene (1/30 mol.) was measured at 35°C. and 60°C. by the iodometric method. The results obtained are shown in Fig. 1. The date, given in Fig. 1, indicate that α-naphthoyl peroxide decomposes more rapidly than β-peroxide, accompanied by some extent of induced decomposition. Particularly at 60°C., α-peroxide

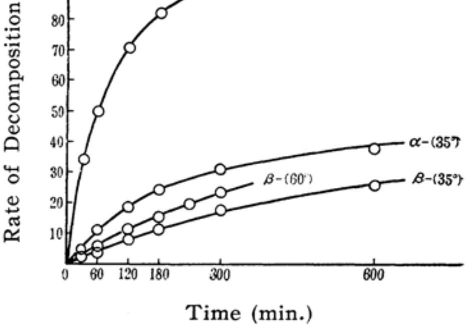

Fig. 1.

---

[1] C. C. Price, "Mechanism of reactions of carbon-carbon double bonds", 70 (1946); W. Cooper, *Nature*, **162**, 897, 927 (1948).

[2] M. Takebayashi and T. Shingaki, This Bulletin, **26**, 137 (1953); M. Takebayashi, T. Shingaki and Y. Ito, ibid., **26**, 475 (1953).

[3] P. D. Bartlett and K. Nozaki, *J. Am. Chem. Soc.*, **69**, 2299 (1947).

[4] L. Horner, *Angew. Chem.*, **61**, 311 (1949); M. Imoto and S. Sai Unpublished; J. Elly, R. N. Haward and W. Simpson, *J. Appl. Chem.*, **1**, 347 (1951).

[5] R. Spolsky et al., *Ind. Eng. Chem.*, **42**, 1847 (1950).

decomposed to the extent of 92 per cent, while β-peroxide to that of only 22 per cent during five hours. The decomposition of β-peroxide was observed to be of nearly first order, and the rate was almost equal to that of benzoyl peroxide at 60°C.

In another experiment, the decomposition products of the peroxides in styrene were examined. It was recongnized that the peroxide decomposed to produce mainly naphthoate radical and naphthyl radical, generating carbon dioxide, and that α-naphthoate radical and β-radical did not isomerize each other during the reaction.[6)]

If the radicals produced from the peroxides are active ones, the rate of polymerization of styrene will be in a parallel relation with that of decomposition of the peroxides. The above expectation was satisfied in the case of the experiments with 1/30 mol. of styrene and 1/6000～1/3000 mol. of the peroxide at 35°C. and 60°C. in the absence of air. The results are summarized in Table I, and a result obtained for benzoyl peroxide is added to it for the sake of comparison.

TABLE I

Peroxide	Temp. (°C.)	React. time (hr.)	Rate of Polymerization (%)
α-Naphthoyl (1/6000 mol.)	35	10	22
β-Naphthoyl (1/6000 mol.)	35	10	4
α-Naphthoyl (1/6000 mol.)	35	26	34
β-Naphthoyl (1/6000 mol.)	35	26	10
α-Naphthoyl (1/6000 mol.)	60	5	22
β-Naphthoyl (1/6000 mol.)	60	5	16
α-Naphthoyl (1/3000 mol.)	60	5	28
β-Naphthoyl (1/3000 mol.)	60	5	20
β-Naphthoyl (1/3000 mol.)	60	18	89
Benzoyl (1/3000 mol.)	60	18	82
None	60	18	1

In the next place, the influence of tertiary amines (1/6000～1/30000 mol.) on the rate of decomposition of the peroxides (1/6000 mol.) in styrene (1/30 mol.) was examined at 35°C. The data obtained are given in Fig. 2 and 3.

Aromatic amines such as dimethyl aniline and ethyl-benzyl aniline, and urotropine accelerate the decomposition of the peroxides remarkably, while heterocyclic amines such as pyridine and quinoline show practically no influence on the rate of the decomposition in the experimental conditions.

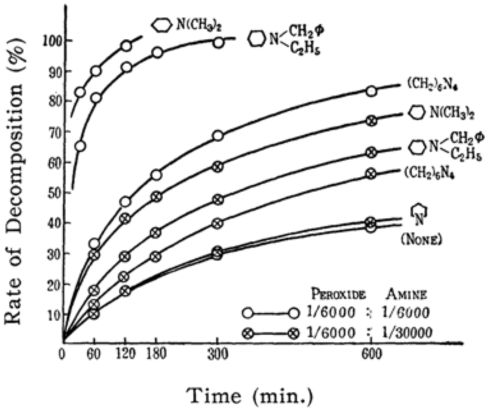

Fig. 2. Rate of decomposition of α-naphthoyl peroxide in the presence of tertiary amines at 35°C.

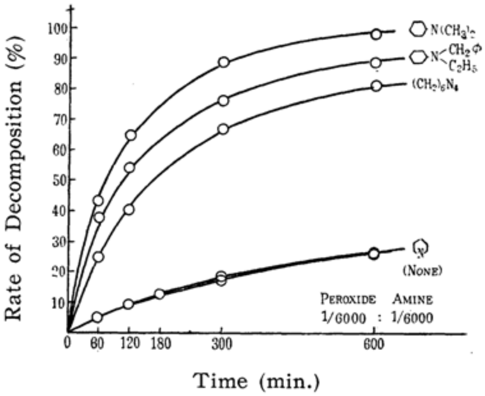

Fig. 3. Rate of decomposition of β-naphthoyl peroxide in the presence of tertiary amines at 35°C.

Then the polymerization of styrene with the peroxides and tertiary amines was carried out at 35°C. in the absence of air. The rate of the polymerization and the degree of it ($\overline{P}$) are listed in Table II.

In the experiments using α-peroxide, the presence of aromatic amines such as dimethyl aniline and ethyl-benzyl aniline, and urotropine show a retarding influence on the rate of polymerization. It has been known that the presence of a little amount of amine accelarates the peroxide-catalyzed polymerization, while a larger amount of amine rather retards.[7)] In an experiment, the polymerization was carried out adding a less amount of amines, but a similar result was obtained. It seems that the amines accelarate the decomposition of peroxide so rapidly that the radicals, produced from the peroxide, react to some extent upon each other or combine with other radicals besides reacting as the initiator of reaction chains.

In the experiments using β-peroxide, on

---

6) Kharasch also has observed this fact in carbon tetrachloride. M. S. Kharash and R. L. Dannley, *J. Org. Chem.*, **10**, 406 (1945).

7) M. Imoto and S. Sai, Unpublished.

TABLE II

In the presence of	React. time (hr.)	Rate of polymerization		$\overline{P}$
		(%)	$v_i \times 10^9$ mol./l., min.	
α-Peroxide (1/6000 mol.)				
Dimethyl aniline (1/30000 mol.)	10	14.3	18	430
α-Peroxide (1/6000 mol.)				
Ethyl-benzyl aniline (1/30000 mol.)	10	17.1	24	400
α-Peroxide (1/6000 mol.)				
Urotropine (1/30000 mol.)	10	17·7	26	380
α-Peroxide (1/6000 mol.)	10	20.3	30	370
α-Peroxide (1/6000 mol.)				
Pyridine (1/6000 mol.)	26	40.9	20	400
α-Peroxide (1/6000 mol.)				
Quinoline (1/6000 mol.)	26	40.5	20	400
α-Peroxide (1/6000 mol.)	26	38	19	410
β-Peroxide (1/6000 mol.)				
Dimethyl aniline (1/6000 mol.)	5	28.9 (60°C.)		
β-Peroxide (1/6000 mol.)				
Ethyl-benzyl aniline (1/6000 mol.)	5	24.9 (60°C.)		
β-Peroxide (1/6000 mol.)				
Dimethyl aniline (1/6000 mol.)	10	16.0	17	520
β-Peroxide (1/6000 mol.)				
Ethyl-benzyl aniline (1/6000 mol.)	10	14.3	14	560
β-Peroxide (1/6000 mol.)				
Urotropine (1/6000 mol.)	10	3.4	1.3	1400
β-Peroxide (1/6000 mol.)	10	4.0	2.0	1100
β-Peroxide (1/6000 mol.)				
Pyridine (1/6000 mol.)	26	10.5	2.2	970
β-Peroxide (1/6000 mol.)				
Quinoline (1/6000 mol.)	26	10.3	2.2	970
β-Peroxide (1/6000 mol.)	26	10.0	2.1	1000

the contrary, dimethyl aniline and ethylbenzyl aniline influence the peroxide, causing it to accelerate the polymerization. The results indicate that the increase of the rate of polymerization is affected not only by the increase of the amount of active radicals, but also by the activity of β-peroxide-radicals on the initiation of the reaction.

Heterocyclic amines such as pyridine and quinoline manifest practically no influence either on the rate of decomposition of peroxides or on that of the peroxide-catalyzed polymerization of styrene.

The accelerating action of aromatic amines on the decomposition of naphthoyl peroxides seems to be elucidated as follows for the case of dimethyl aniline. The decomposition may be initiated by the addition of dimethyl aniline with its lone-pair of electrons on nitrogen atom to the positively polarized part of the peroxide, giving rise to the formation of an iminium salt.[8] The salt may decompose to produce radicals: RCOO$\cdot$and R$\cdot$ (R indicates naphthyl radical), ions: $RCOO^+$ and $RCOO^-$, and a radical-cation of dimethyl aniline. Here the radicals, RCOO$\cdot$ and R$\cdot$, initiate the polymerization, and sometimes react on the peroxide, amine or other radicals. The anion $RCOO^-$ probably forms RCOOH with H^+, and the radical-cation dimerizes giving out H^+, or comes into play for the polymerization.[9]

Heterocyclic amines showed practically no influence on the decomposition of the peroxides in the experimental conditions. However, it has been reported that the decomposition of benzoyl peroxide is accelerated in pyridine.[10] Therefore, the concentration of amine in reaction systems might come in question,

Pyridine, contrary to dimethyl aniline, can hardly be added with its nitrogen atom to naphthoyl peroxide owing to the steric

---

[8] L. Horner and K. Scherf, *Ann.*, **573**, 35 (1951).

[9] L. Horner and E. Schwenk, *Ann.*, **566**, 69 (1950).

[10] K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **78**, 1686 (1946).

strain[11] between them. If the decomposition should be accelerated by pyridine the reaction might be induced by the mutual interaction between pyridine and peroxide radicals.

Experimental

Materials—For the preparation of α-naphthoyl peroxide a modification of the method used by Kharasch and Dannley[6] was found to be useful. α-Naphthoyl chloride was dissolved in 40 cc. of anhydrous toluene; the solution was then added slowly to a vigorously stirred solution of 5 g. of sodium peroxide in 50 cc. of cold water. The temperature was not allowed to rise above 0°C. The stirring at 0° C. was continued for about three hours. Then the α-naphthoyl peroxide separated out as a pale precipitate. The precipitate was collected on a filter, washed with water, and dried. It was then dissolved in chloroform and fractionally precipitated by pouring the solution into methanol on stirring. The procedure was repeated several times. Yield: 55 %. The purity was found to be of 90 per cent by titration. A pure sample decomposed sharply at 98°C. The preparation of β-peroxide was similar to that of α-peroxide, the temperature of the reaction being held at 5∼7° C. Yield: 76 %. A sample, the peroxide content of which was 95 %, decomposed sharply at 138° C..

The styrene employed was distilled with steam, dried over a small amount of calcium chloride, and was distilled under reduced pressure just before use. B.p. 63°C./55 mm. The absence of peroxides was ascertained by the test with ferrous ammonium sulfate and ammonium thiocyanate. The aromatic and heterocyclic amines employed were distilled under reduced pressure just before use.

Decomposition of Peroxides—The decomposition of peroxide was carried out in sealed reaction tubes. The tubes were treated with warmed cleaning solution for several hours, left standing in a dilute solution of sodium bisulfate for a short time, then rinsed with distilled water, and dried. The definite amount of the peroxide and amine were mixed with 1/30 mol. of styrene in the reaction tube, the tube was cooled in an ice-salt-bath, then was evacuated and sealed off. The sealed tube was immersed in a thermostat. After the required time the tube was cooled again, and opened. The content of the tube was mixed with 40 cc. of purified acetone in a glass-stoppered flask, and then titrated by the standard solution (1/10N) of sodium thiosulfate according to the direction of Blomquist and Buselli.[12] It was ascertained that no reaction took place between iodine and amine during the titration.

Polymerization of Styrene — The definite amount of the peroxide and amine were mixed with 1/30 mol. of styrene in a reaction tube, evacuated as described above, and then immersed in a thermostat for the reaction time. When the reaction time was over, the tube was cooled in an ice-salt-bath. The reaction products were dissolved in benzene, the polymer produced was precipitated by adding methanol to the solution, and the weight of polystyrene was measured. The molecular weight of the polymer was determined by the viscosity method.

Summary

(1) The rates of polymerization of styrene with α-and β-naphthoyl peroxide have been found to be in a parallel relation with the rates of decomposition of the peroxides at 35° and 60°C.

(2) Aromatic amines such as dimethyl aniline and ethyl-benzyl aniline, and urotropine accelerate the decomposition of the peroxides.

(3) In the experiments using α-peroxide, the presence of the aromatic amines and urotropine show a retarding influence on the rate of the polymerization. In the experiments using β-peroxide, on the contrary, dimethyl aniline and ethyl-benzyl aniline influence the peroxide to accelerate the polymerization.

(4) Heterocyclic amines such as pyridine and quinoline manifest practically no influence either on the rate of decomposition of the peroxides or on that of the peroxide-catalyzed polymerization of styrene.

(5) In respect to the action of amines, a tentative theory has been made.

The authors express their hearty thanks to the Ministry of Education for a Grant in Aid for Scientific Research.

Chemical Laboratory, South College,
Osaka University, Osaka

---

[11] H. C. Brown et al., *J. Am. Chem. Soc.*, **64**, 374, 378, 1452 (1945), ibid., **64**. 325 (1942), ibid., **70**, 2878 (1948), ibid., **71**, 445 (1949).

[12] A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951).