The Catalytic Action of Organic Peroxides on the Polymerization of Ethenoid Compounds. I. The Activity of Substituted Benzoyl Peroxides in the Polymerization of Styrene

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It is possible from a study of the catalyzed polymerization of vinyl compounds to obtain information on the activity of the radicals derived from peroxides initiating the polymerization. Cooper⁽¹⁾, studying the polymerization of styrene with various types of substituted benzoyl peroxide has observed that electron-attracting substituents give radicals of lower activity, while electron-repelling ones increase the activity of the radicals. However, the velocity of initiation of catalyzed polymerization is affected not only by the activity of radicals, but also by the amount of active radicals which are produced in a unit of time. Therefore the velocity of decomposition of peroxides also seems to be an important factor. Swain and his co-workers⁽²⁾ have reported that electron-attracting substituents retard the reaction and electron-repelling groups accelerate in the unimolecular thermal decomposition of *m*- and *p*- substituted benzoyl peroxides, and that the data fit the Hammett equation closely. Blomquist and Buselli⁽³⁾, however, have indicated that the homolytic cleavage of symmetrical benzoyl peroxides into free radicals may involve the interaction of two opposing dipoles.

The present study was initiated to see the relation between the amount and the activity of the radicals initiating the polymerization of styrene. For this purpose, symmetrical *m*- and *p*- substituted benzoyl peroxides were taken up as the catalyst.

As an empirical measure of the activities of peroxides, styrene (1/30 mol.) was polymerized with various types of substituted benzoyl peroxide (1/3000 mol.) at 60°C. for eighteen hours in the absence of air, and the effects of peroxides on the rate of polymerization have been measured. The results obtained are summarized in Table 1.

Table 1

Substituted benzoyl peroxide	Rate of polymerization (%)	K of substituted benzoic acid at 25°C. ($\times 10^{-5}$)
p, *p*′-Dimethoxy	99.8	3.2
m, *m*′-Dimethoxy	85.7	5
p, *p*′-Dimethyl	91.6	4.4
m, *m*′-Dimethyl	82.0	5.6
Unsubstituted	81.5	6.69
p, *p*′-Dichloro	71.9	9.3
m, *m*′-Dichloro	57.3	15.5
p, *p*′-Dicyano	28.3	23.5
m, *m*′-Dicyano	31.5	19.9
p, *p*′-Dinitro	10.1	39.6
m, *m*′-Dinitro	11.2	34.5
None	1.5	

This experiment shows that the activities of the substituted benzoyl peroxides on the rate of polymerization of styrene are inversely proportional to the square root of the dissociation constants K of the corresponding substituted benzoic acids, and that better linearity is found when using $\sqrt{K}$ than when using Hammett's constant σ as shown in Fig. 1.

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(1) W. Cooper, *Nature*, **162**, 897 (1948).

(2) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5126 (1950).

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

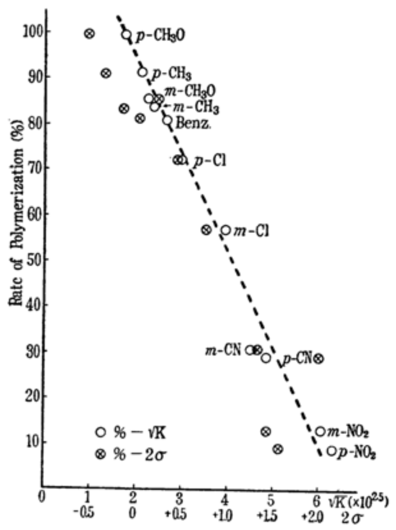

Fig. 1.

In order to elucidate the results described above, the authors observed, in the first place, the rate of decomposition of the peroxides in styrene at 60°C. for eighteen hours. The percentage of decomposition is plotted against $\sqrt{K}$ or 2σ in Fig. 2. This has been included as it shows that the rate of decomposition is inversely proportional to $\sqrt{K}$ and proportional to 2σ, and that better linearity is found with $\sqrt{K}$ than with 2σ.

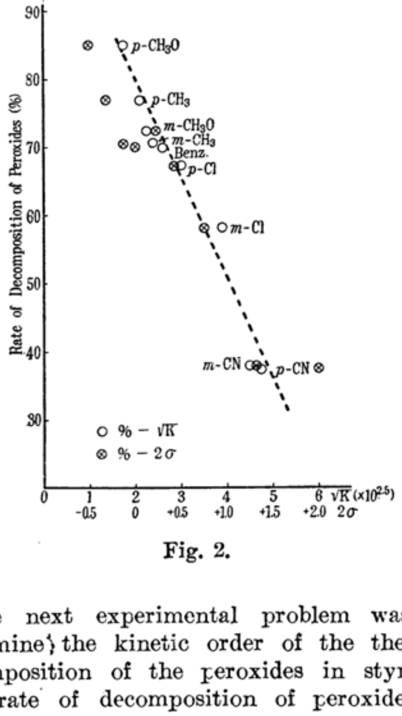

Fig. 2.

The next experimental problem was to determine the kinetic order of the thermal decomposition of the peroxides in styrene. The rate of decomposition of peroxides in solution is given generally by

$$-d[P]/dt=k_1[P]+k_t[P]^n,$$

where P expresses the concentration of the undecomposed peroxide, k_1 the rate constant of unimolecular decomposition, k_t that of induced decomposition, and n the kinetic order of induced decomposition.

The experiments with benzoyl peroxide and some substituted benzoyl peroxides (1 mol. % to styrene) were carried out at 60°C. The percentage of decomposition of peroxides was determined by the iodometric method according to the direction of Swain⁽²⁾. As for dinitrobenzoyl peroxides, the rate of decomposition was not measured exactly by this method because nitrobenzoic acids, produced during the reaction, had also an oxidizing action. The data are given in Fig. 3 and Table 2. The decomposition was observed to be of first order in all cases. Therefore, it should be possible to ignore the term for the bimolecular induced chain decomposition⁽⁴⁾. Then, we have

$$-d[P]/dt=k_1[P].$$

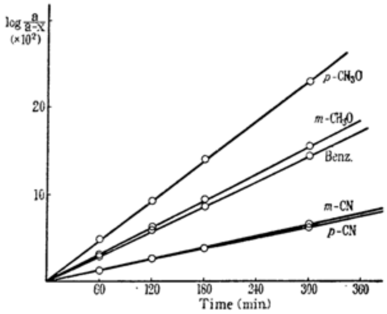

Fig. 3.

Table 2

Peroxide	$k_1\times10^4$, min.$^{-1}$	$\log(k/k_0)$
p,p'-Dimethoxy-benzoyl	17.7	0.206
m,m'-Dimethoxy-benzoyl	12.0	0.033
p,p'-Dimethyl-benzoyl	12.7	0.061
m,m'-Dimethyl-benzoyl	11.3	0.009
Benzoyl	11.05	0.000
p,p'-Dichloro-benzoyl	9.9	−0.047
m,m'-Dichloro-benzoyl	8.1	−0.135
p,p'-Dicyano-benzoyl	4.6	−0.380
m,m'-Dicyano-benzoyl	4.8	−0.362

Table 2 indicates also that the greater the electron-affinity of substituentsis, the more

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(4) Swain has obtained a different result in the thermal decomposition of benzoyl peroxide in styrene. His rate curve for decomposition shows a marked autocatalysis, which he has supposed to be due to overheating.

rapidly the peroxides decompose in styrene. The relation between $\log(k/k_0)$ and the rate of polymerization is shown in Fig. 4, where k indicates the rate constant of substituted benzoyl peroxides, and k_0 that of unsubstituted ones. It is recognized that the rate of decomposition of peroxides is in a parallel relation with the rate of polymerization of styrene.

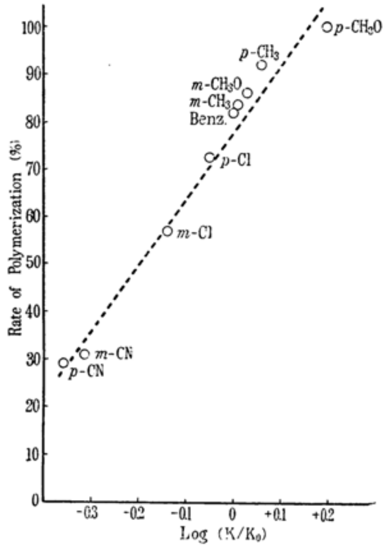

Fig. 4.

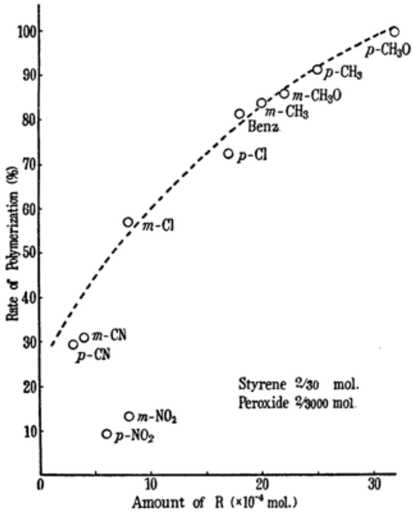

Fig. 5.

Considering that the thermal decomposition of peroxides in styrene is an unimolecular reaction, it is supposed that the radicals acting as the initiator of the polymerization are chiefly benzoate radical RCOO and aryl radical R, produced from the radical RCOO, and that the larger the amount of the radicals which are produced in unit time, the greater the rate of polymerization of styrene. The amounts of various types of the radical R were estimated from those of the carbon dioxide which was generated. Then, the above expectation seems to be satisfied about the radical, R, excepting the cases of dinitrobenzoyl peroxides, as shown in Fig. 5. Concerning this subject, furthermore, the kinetic studies on the formation of carbon dioxide are under way.

In respect to the small activity of dinitrobenzoyl peroxides, a consideration has been deduced. Assuming that the segments of the peroxides form nitrobenzene and nitrobenzoic acids during the polymerization, it might be expected that these nitro-compounds would react as inhibitors of the polymerization⁽⁵⁾.

It is possibly owing to the inhibiting action of the nitro-compounds described above that the rate of polymerization with dinitrobenzoyl peroxides is quite small in spite of the comparatively large rate of decomposition⁽³⁾.

Experimental

Materials.—The styrene employed was distilled with steam, dried over small amount of calcium chloride, and 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. All substituted peroxides were prepared by the reaction of a solution of an acid chloride in dry toluene with an excess of aqueous sodium peroxide according to the method of Price and Krebs⁽⁶⁾ used for p,p'-dinitrobenzoyl peroxide. In general, the melting points or decomposition points were quite sharp after recrystallization

Table 3

Peroxide	M. p. (Dec.) (°C.)	Purity (%)
p,p'-Dimethoxy-benzoyl	128	98.5
m,m'-Dimethoxy-benzoyl	82	99.0
p,p'-Dimethyl-benzoyl	136	98.3
m,m'-Dimethyl-benzoyl	54	99.0
Benzoyl	106—107	98.2
p,p'-Dichloro-benzoyl	140	99.0
m,m'-Dichloro-benzoyl	123	98.4
p,p'-Dicyano-benzoyl	176	98.0
m,m'-Dicyano-benzoyl	163	96.7
p,p'-Dinitro-benzoyl	158	99.1
m,m'-Dinitro-benzoyl	137	98.0

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(5) S. Okamura, K. Uno and K. Yamamoto, read at the fifth annual meeting of the Chemical Society of Japan, April 4, 1952; C. C. Price, "Mechanism of Reactions at Carbon-Carbon Double Bonds", New York, 1946, p. 87.

(6) C. C. Price and E. Krebs, "Organic Syntheses", **23**, 65 (1943).

from hydrocarbon solvents, and represented to a fair extent the purity of the peroxide. In Table 3 are listed the substituted benzoyl peroxides employed in this study.

Polymerization of Styrene.—The polymerization of styrene was carried out in sealed 17 cc. reaction tubes. The tubes were treated with warmed cleaning solution for several hours, left standing in a very dilute solution of sodium bisulfate for a short time, then rinsed with distilled water, and dried. A peroxide (1/3000 mol.) was mixed with 1/30 mol. of styrene in the reaction tube, the tube cooled in an ice-salt-bath, then evacuated and sealed off. The sealed tube was warmed to room temperature and then immersed in a 60 ± 0.05°C. thermostat for eighteen hours, then removed and cooled in an ice-salt-bath. Unchanged styrene was driven off in a vacuum and the weight of polystyrene was measured. In another experiment, the reaction products were dissolved in benzene and the polymer produced was precipitated by adding methanol to the solution. The weight of polystyrene was almost equal to that of the case mentioned above.

Decomposition of Peroxides.—The apparatus is shown schematically in Fig. 6. A is the reaction tube of 22 mm. diameter and 35 cc. capacity, B the inlet tube of 7 mm. diameter for nitrogen, C the cooler with cold water, and D the soda-lime tube for the absorption of the carbon dioxide which is generated. B was connected with the source of purified nitrogen. During the reaction a soda-lime tube E was attached to D.

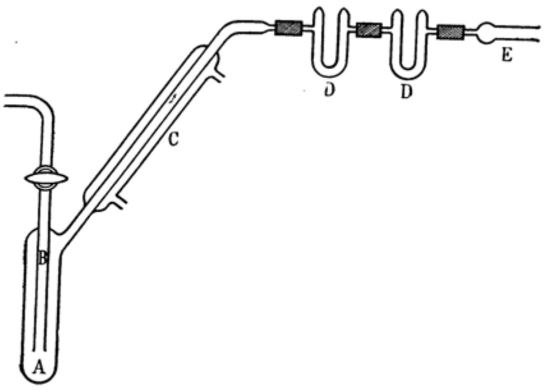

Fig. 6.

A mixture of peroxide (2/3000 mol.) and styrene (2/30 mol.) was taken in A and the tube A was cooled in an ice-salt-bath. Pure nitrogen(7) was passed through B into the whole apparatus. When the air in the apparatus was driven out, namely the weight of D had no longer increased, A was warmed to room temperature and then immersed in a $60-0.05$°C. thermostat for eighteen hours. The reaction was carried out in a slow stream of nitrogen. After the required time, A was cooled, passing through nitrogen for one hour, and the weight of carbon dioxide absorbed in D was measured. In the experiments with peroxides such as benzoyl peroxide and dimethyl- and dichloro-benzoyl peroxide, the contents of A were dissolved in 30 cc. of benzene and hydrolyzed for twenty eight hours with 50 cc. of water and 4 g. of sodium hydroxide. The products were found to be chiefly the corresponding benzoic acids.

Summary

(1) The rates of polymerization of styrene with *m*- and *p*-substituted benzoyl peroxides have been found to be inversely proportional to the square root of the dissociation constants of the corresponding substituted benzoic acids.

(2) The thermal decomposition of the peroxides in styrene has been observed to be of first order in all cases.

(3) It has been found that the rate of decomposition of peroxides is in a parallel relation with the rate of polymerization of styrene.

(4) The relation between the amounts of radicals derived from the peroxides and the rates of polymerization has been studied.

(5) In respect to the small activity of dinitro-benzoyl peroxides, a tentative theory has been made.

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(7) Purified by the method described in L. F. Fieser, "Experiments in Organic Chemistry", 2nd Ed., New York, 1941, p. 395.