The Catalytic Action of Organic Peroxides on the Polymerization of Ethenoid Compounds. II. The Activity of Substituted Benzoyl Peroxides on the Polymerization of Vinyl Acetate

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In the previous work1) of this series it was established that the activity of symmetrical *m*- and *p*-substituted benzoyl peroxides on the mean velocity of polymerization of styrene is inversely proportional to the square root of the dissociation constants of the corresponding substituted benzoic acids,* and that the rate of polymerization is in a parallel relation

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1) M. Takebayashi and T. Shingaki, This Bulletin, **26**, 137 (1953).

*) The mean velocity of polymerization was measured after eighteen hours at 60° C.

to the rate of decomposition of the peroxides. The present paper is concerned with a comparative investigation of the activity of the peroxides on the polymerization of vinyl acetate and of styrene.

The polymerization of vinyl acetate has been carried out with 1/30 mol. of vinyl acetate and 1/3000 mol. of symmetrical *m*- and *p*-substituted benzoyl peroxides at 40°C. and 60°C. in the absence of air, and the effect of peroxides on the rate of polymerization has been measured. The results obtained are summarized in Table 1. In Fig. 1, the over-all velocity (v_{Br}) of polymerization is plotted against the square root of the dissociation constants (K) of the corresponding substituted benzoic acids.

Table 1

Rate of Polymerization of Vinyl Acetate

Substituted benzoyl peroxide	Rate of polymerization (%)		$v_{Br}\times10^3$, mol./l., min.	
	at 40°C., for 18 hrs.	at 60°C., for 2 hrs.	at 40°C.	at 60°C.
p,p'-Dimethoxy	99.9	98.3	9.91	87.8
m,m'-Dimethoxy	45.2	87.1	4.49	77.8
p,p'-Dimethyl	49.8	96.8	4.94	86.5
m,m'-Dimethyl	37.0	91.4	3.67	81.6
Unsubstituted	46.2	92.0	4.58	82.2
p,p'-Dichloro	31.4	83.8	3.12	74.8
m,m'-Dichloro	6.6	16.8	0.66	15.0
p.p'-Dicyano	4.1	9.0	0.41	8.0
m,m'-Dicyano	3.4	5.9	0.34	5.3
p,p'-Dinitro	0.7	2.4	0.07	2.1
m,m'-Dinitro	1.0	3.6	0.10	3.2
None	0.0	0.3		

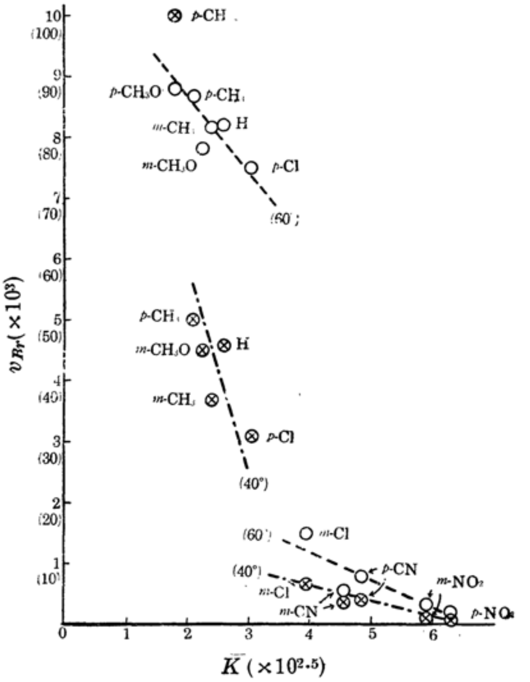

Fig. 1.—Polymerization of vinyl acetate in the presence of substituted benzoyl peroxides at 40°C. and 60°C.

* The numbers in parentheses are those for the data at 60°C.

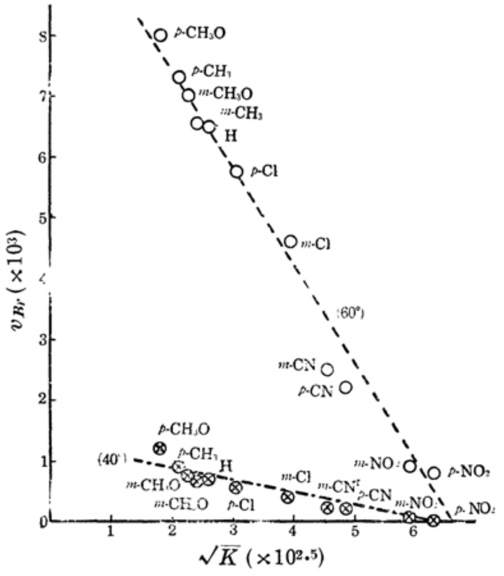

Fig. 2.—Polymerization of styrene in the presence of substituted benzoyl peroxides at 40°C. and 60°C.

Table 2

Rate of Polymerization of Styrene

Substituted benzoyl peroxide	Rate of polymerization (%)		$v_{Br}\times 10^3$, mol./l., min.	
	at 40°C., for 70 hrs.	at 60°C.,* for 18 hrs.	at 40°C.	at 60°C.
p,p'-Dimethoxy	59.1	99.8	1.18	7.98
m,m'-Dimethoxy	36.9	85.7	0.74	6.85
p,p'-Dimethyl	44.3	91.6	0.89	7.32
m,m'-Dimethyl	33.1	82.0	0.66	6.56
Unsubstituted	35.1	81.5	0.70	6.52
*p,p'*Dichloro	28.6	71.9	0.57	5.75
m,m'-Dichloro	22.3	57.3	0.45	4.58
p,p'-Dicyano	10.3	28.3	0.21	2.26
m,m'-Dicyano	9.7	31.5	0.19	2.52
p,p'-Dinitro	1.4	10.1	0.03	0.81
m,m'-Dinitro	3.1	11.2	0.06	0.89
None	1.1	1.5		

* The data at 60°C. are quoted from the previous paper.

Comparing the results with those obtained in the polymerization of styrene, which are shown in Table 2 and Fig. 2, remarkable differences are recognized in the activity of peroxides and the velocity of polymerization.

In the polymerization of vinyl acetate the peroxides are divided into two groups according to their activities, the one containing effective peroxides, such as dimethoxy-, dimethyl-and *p,p'*-dichloro-benzoyl peroxides,and the other less effective ones, such as *m,m'*-dichloro-, dicyano-, and dinitro-benzoyl peroxides. And the activity of peroxides in each group is nearly inversely proportional to $\sqrt{K}$ at the experimental conditions (Fig. 1), while in the polymerization of styrene the same relation has been satisfied for all peroxides used (Fig. 2).

The polymerization of vinyl acetate proceeded more rapidly than that of styrene, as had been reported.[2] This tendency was observed to be remarkable in the presence of effective peroxides, where the velocity of polymerization of vinyl acetate was found to be about six[3] and over ten times as large as that of styrene at 40°C. and 60°C., respectively. While in the presence of less effective peroxides, the velocity of polymerization of vinyl acetate was observed to be only about two and three times as large as that of styrene at 40°C. and 60°C., respectively.

In the next place, the authors investigated the kinetic order of the thermal decomposition of the peroxides in vinyl acetate at 40°C. and 60°C. by the iodometric method according to the direction of Swain and his co-workers.[4] The decomposition was observed to be of first order at 40°C., but not always exactly so at 60°C. perhaps because of the fact that the polymerization proceeded so rapidly that the condition of decomposition of the peroxides was changed to some extent during the reaction. The rate constant (k_1) is given in Table 3, and that (k_1') in styrene is added in it for the sake of comparison.

Table 3

Rate Constant of Decomposition of Substituted Benzoyl Peroxides

Substituted benzoyl peroxide	$k_1\times 10^4$, min.$^{-1}$		log (k/k_0)		$k_1'\times 10^4$, min.$^{-1}$
	at 40°C,	at 60°C.	at 40°C.	at 60°C.	at 60°C.
p,p'-Dimethoxy	7.36		0.25		17.7
m,m'-Dimethoxy	3.91	34	−0.02	0.0	12.0
p,p'-Dimethyl	4.60		0.05		12.7
m,m'-Dimethyl	2.99	34	−0.14	0.0	11.3

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[2] For examples: G. V. Schulz and E. Husemann, *Z. physik. Chem.* (B) **39**, 246 (1938); A. C. Cuthbertson, G. Gee and E. K. Rideal, *Proc. Royal Soc.* A, **170**, 300 (1939); G. M. Burnett, *Quarterly Revs.* **4**, 292 (1950).

[3] Only in the presence of *p,p'*-dimethoxy-benzoyl peroxide, the polymerization velocity of vinyl acetate was found to be about nine times as large as that of styrene at 40°C.

[4] C. G. Swain, W. H. Stockmayer and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

Unsubstituted	4.14	34	0.00	0.0	11.05
p,p'-Dichloro	2.14	18	−0.30	−0.27	9.9
m,m'-Dichloro	1.61	3.2	−0.41	−1.03	8.1
p,p'-Dicyano	0.70	1.8	−0.77	−1.28	4.6
m,m'-Dicyano	0.69	1.8	−0.78	−1.28	4.8

The data given in Table 3 indicate that the greater the electron-repelling effect of substituents, the more rapidly the peroxides decompose in vinyl acetate as well as in styrene, and that the effective peroxides decompose about two to three times more rapidly in vinyl acetate than in styrene at 60°C., while less effective ones decompose about two or three times more slowly, suggesting the solvent effect. Fig. 3 shows the relation between the velocity of polymerization of vinyl acetate and log (k/k_0), where k_0 and k are the rate constants of benzoyl peroxide and substituted benzoyl peroxides, respectively.

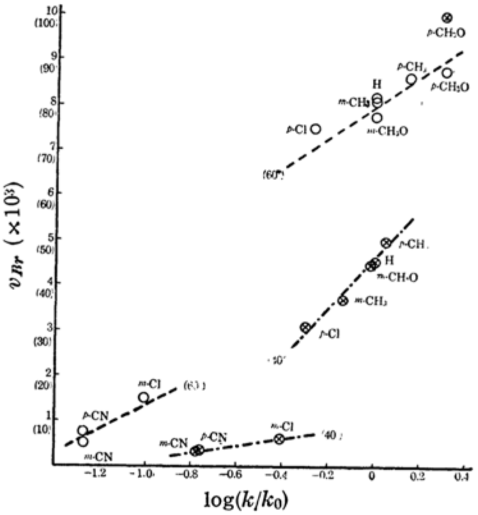

Fig. 3.—Correlation of extrapolated first order rate constants with v_{Br} in vinyl acetate at 40°C. and 60°C.

* The numbers in parentheses are those for the data at 60°C.

The results indicate also that the peroxides are divided into two groups according to their activities, contrary to the results obtained in the polymerization of styrene, and that the activity of peroxides in each group is nearly proportional to log (k/k_0). The above facts lead us to the reasoning that the velocity of polymerization is affected not only by the rate of decomposition of peroxides but also by the activity of radicals derived from peroxides.

Considering that the thermal decomposition of peroxides in vinyl acetate is an uni-molecular reaction, the radicals acting as the initiator of the polymerization are suggested to be various kinds of benzoate radical RCOO and of aryl radical R, produced by loosing carbon dioxide from the radical RCOO. Then the authors measured the amount of carbon dioxide generated from the peroxides (2/3000 mol.) in vinyl acetate (2/30 mol.).

In the experiments at 40°C. for eighteen hours, carbon dioxide was not generated from all the peroxides except *p,p'*-dimethoxy-benzoyl peroxide. Therefore, it is supposed that the radical acting as the initiator is chiefly RCOO, except in the case of *p,p'*-dimethoxy-benzoyl peroxide. The effects of various kinds of radical RCOO, which should be produced from the peroxides, on the velocity of polymerization were estimated per mol. of RCOO as shown in Table 4.

Table 4

Effect of the Radical RCOO on the Polymerization

Substituted benzoyl peroxide	Extent of decomposition (%)	Amount (M) of RCOO ($\times 10^{-4}$ mol.)	v_{Br}/M (mol./l., min.)
*m,m'*Dimethoxy	34	2.3	0.19
p,p'-Dimethyl	39	2.6	0.19
m,m'-Dimethyl	28	1.9	0.19
Unsubstituted	36	2.4	0.19
p,p'-Dichloro	21	1.4	0.21
m,m'-Dichloro	16	1.0	0.06
p,p'-Dicyano	7	0.5	0.08
m,m'-Dicyano	7	0.5	0.07

The data in Table 4 lead us to the conclusion that there are two groups in the activity of the radical RCOO. From *p,p'*-dimethoxy-benzoyl peroxide 5×10^{-4} mol. of carbon dioxide was produced. The conspicuous effect of the peroxide on the velocity of polymerization is supposed to depend on the activities of *p*-methoxy-benzoyl and *p*-methoxy-phenyl radicals besides the large rate of decomposition of the peroxide.

In the experiments at 60°C. for two hours, on the contrary, carbon dioxide was generated from effective peroxides, not from less effective ones. The result also suggests that two types of radical, RCOO and R, react as the initiator in the presence of effective peroxides, while the radical RCOO reacts chiefly in the presence of less effective ones. The amounts of carbon dioxide generated are listed in Table 5.

Table 5

Amount of Carbon Dioxide Generated from Peroxides at 60°C.

Substituted benzoyl peroxide	Amount of carbon dioxide ($\times 10^{-4}$ mol.)
p,p'-Dimethoxy	6.8
m,m'-Dimethoxy	3.0
p,p'-Dimethyl	4.5
$m,'m$-Dimethyl	3.2
Unsubstituted	3.3
p,p'-Dichloro	2.7

The data are in a similar order to those found for the velocity of polymerization at 60°C. in the presence of effective peroxides.

Experimental

Materials.—The vinyl acetate employed was washed several times with water[5], dried over anhydrous sodium sulfate, and fractionated in the atmosphere of nitrogen just before use. b.p. 72°C. All substituted benzoyl peroxides were prepared and purified as described in the previous paper.[1]

Polymerization of Vinyl Acetate.—A peroxide (1/3000 mol.) and vinyl acetate (1/30 mol.) were taken in the reaction tube, the tube cooled in a mixture of solid carbon dioxide and alcohol, and sealed off in a vacuum. The sealed tube was immersed in a thermostat of 40°C. or 60°C. for the reaction time, then removed and cooled in an ice-salt-bath. Unchanged vinyl acetate was driven off in a vacuum and the weight of poly-vinyl acetate was measured. In another experiment, the reaction products were dissolved in acetone and the polymer was precipitated by adding water to the solution. The weight of polyvinyl acetate was almost equal to that of the case mentioned above.

Decomposition of Peroxides.—Owing to the high-volatility of vinyl acetate, the apparatus and experimental procedure were somewhat modified compared with those in the case of the decomposition in styrene. The main part of the apparatus is shown in Fig. 4.

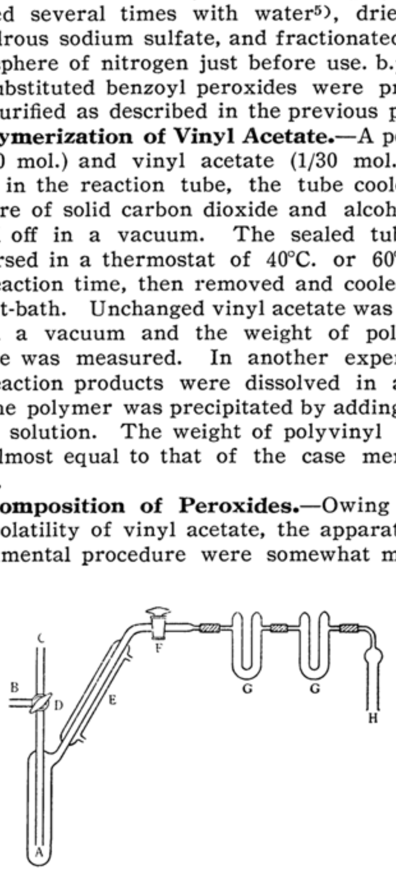

Fig. 4

A is the reaction tube of 22 mm. diameter and 35 cc. capacity, B the inlet tube for nitrogen, C the tube for evacuation, E the cooler with cold water, and G the soda-lime tube for the absorption of carbon dioxide produced. During the reaction a soda-lime tube H was attached to G.

A mixture of peroxide (2/3000 mol.) and vinyl acetate (2/30 mol.) was taken in A and tube A was cooled in solid carbon dioxide and alcohol. After the cock F was closed and the reaction tube evacuated through C, the cock D was closed. Then the tube A was immersed in a thermostst of 40°C. or 60°C. for the reaction time. When the requied time was over, A was cooled again at –30∼35°C. in a mixture of solid carbon dioxide and alcohol, the cock F opened, passing pure nitrogen through B into the whole apparatus, and the weight of carbon dioxide absorbed in G was measured. The amount of carbon dioxide was verified by the blank test.

Summary

(1) The activity of symmetrical m- and p-substituted benzoyl peroxides on the rate of polymerization of vinyl acetate has been investigated at 40°C. and 60°C. in the absence of air.

(2) The peroxides have been divided into two groups according to their activities. The activity of peroxides in each group is nearly inversely proportional to the square root of the dissociation constants of the corresponding substituted benzoic acids in the experimental conditions.

(3) The thermal decomposition of the peroxides in vinyl acetate has been observed to be of first order at 40°C., but not always exactly so at 60°C.

(4) In the decomposition of the peroxides at 40°C., carbon dioxide was not generated from all the peroxides excluding p,p-dimethoxybenzoyl peroxide; while in the decomposition at 60°C., carbon dioxide was produced from effective peroxides, such as dimethoxy-, dimethyl-, and p,p'-dichloro-benzoyl peroxides.

(5) It has been confirmed that the velocity of the polymerization is affected not only by the rate of decomposition of the peroxides but also by the activity of radicals derived from the peroxides.

(6) The results have been compared with those obtained in the polymerization of styrene.

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[5] S. Okamura, "*Kobunshi-tembo,*" **2**, 125 (1950).