determination of this material was made by saponification of a 1.71-g. aliquot of IIa to produce 0.57 g. of benzoic acid and 1.03 g. of a phenolic component. Recrystallization of the phenolic component from chloroform gave 0.85 g. of pure 1-nitro-4-naphthol, m. p. 164–165° (lit.[19] 164°); benzoate m. p. 176–177° (lit.[20] 176°). The isolation of 0.25 g. of 1-nitro-2-naphthol and 0.85 g. of 1-nitro-4-naphthol proved that fraction II contained a minimum of 8.3% and a 58.3% of the respective benzoate esters.

Saponification of III produced 0.42 g. of benzoic acid and 0.64 g. of a phenol. Purification of the phenol by decolorizing an alkaline solution with charcoal and precipitation with acetic acid gave 0.57 g. of 1-nitro-5-naphthol, m. p. 170–171° (lit.[21] 171°); methyl ether, 95–96° (lit.[21] 96–97°). The 0.57-g. yield of pure phenol proved that 66% of III consisted of 1-nitro-5-benzoyloxynaphthalene.

Discussion.—The yields of products are listed in Table I. The quantities of carbon dioxide and benzene are of limited accuracy but are included because, as they are of similar magnitude, they indicate that the free phenyl radicals which did form probably produced benzene and did not substitute the aromatic nucleus.

Table I

Product	Moles of products per mole of $(C_6H_5COO)_2$ 1-$BrC_{10}H_7$	1-$ClC_{10}H_7$	1-$NO_2C_{10}H_7$
CO_2	0.01	0.02	0.03
C_6H_5COOH	.98	.91	.92
C_6H_6	.03	.07	.01
1,2-Ester	.007	.009	.03
1,4-Ester	.41	.16	.18
1,5-Ester	.20	.14	.10

The formation of quantities of esters is unusual, for in general the decomposition of benzoyl peroxide in aromatic solvents produces phenylated products.[22] Substitution by aroyloxy radicals is not unknown, however, for the decomposition of benzoyl peroxide in phenols[23] results in substitution by the benzyloxy group. Also, the decomposition of α-naphthoyl peroxide in carbon tetrachloride[24] produces some 4-α-naphthoyloxy-1-naphthoic acid. As the benzoyloxy radical is a logical precursor to the phenyl radical, it seems possible that benzoyloxylation occurs with nuclei highly susceptible to free radical attack while phenylation occurs with less reactive substances.

Direct comparison of the sum of the moles of 1,2-ester and 1,4-ester to the moles of 1,5-ester gives the following relative activating influences toward benzoyloxy free radical attack: NO_2, 19 > Br, 2.0 > Cl, 1.2 > H, 1.0. As these values are based on yields of only 31–62% identified products, their accuracy does not warrant including corrections for the number of positions available for substitution in the two rings.

Cleveland 6, Ohio Received April 23, 1951

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[Contribution from the Institute of Polymer Research, Polytechnic Institute of Brooklyn]

Allyl Polymerization. II. Decomposition of Benzoyl Peroxide in Allyl Esters[1,2]

By Norman G. Gaylord[3] and Frederick R. Eirich

The decomposition of benzoyl peroxide in the course of the bulk polymerization of allyl esters is almost first order, the rate constant increasing with increasing initial peroxide concentration. The order of rate of decomposition in the allyl esters is trimethylacetate > propionate > acetate > ethyl carbonate. It is suggested that the chain reaction accompanying the spontaneous unimolecular decomposition may involve products arising from, in addition to attack upon α-methylenic hydrogen, an attack on the acyl group of the esters as well as from a free radical displacement reaction on the allylic carbon causing cleavage of the carbon–oxygen bond, particularly in the case of allyl trimethylacetate.

In a previous paper[4] it was shown that the decomposition of benzoyl peroxide in allyl alcohol and allyl bromide, as in other solvents,[5] can be considered as a spontaneous first-order reaction accompanied by a free radical induced chain decomposition. This results in a variation of the rate of decomposition with the initial concentration of peroxide.[5a,c,d,6,7] The rates of decomposition in solutions containing polymerizable monomers are generally increased over those in the non-polymerizing solvent alone[8,9] although it is reported[5d] that 3,4-dichlorostyrene suppresses induced decomposition with a resultant lowered rate of decomposition. The present work reports an investigation of the decomposition of benzoyl peroxide in the course of the bulk polymerization of several allyl esters.

Results and Discussion

Decomposition in Allyl Esters.—The decomposition of benzoyl peroxide was followed as a function of time during the bulk polymerization of several allyl esters at 80° under vacuum, in the presence of various initial concentrations of peroxide. Peroxide concentrations were determined by iodometric titration as described in the Experimental section and are expressed in moles per kilo-

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[1] This work was carried out with the support of the U. S. Navy, Bureau of Aeronautics.

[2] Abstracted from a portion of the dissertation submitted by Norman G. Gaylord to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

[3] E. I. du Pont de Nemours and Co., Yerkes Research Laboratory, Buffalo, N. Y.

(4) Part I of this series: This Journal, **73**, 4981 (1951).

(5) (a) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946); (b) W. E. Cass, *ibid.*, **68** 1976 (1946); (c) B. Barnett and W. E. Vaughan, *J. Phys. Colloid Chem.*, **51**, 926, 942 (1947); (d) C. G. Swain, W. H. Stockmayer and J. T. Clarke, This Journal, **72**, 5426 (1950).

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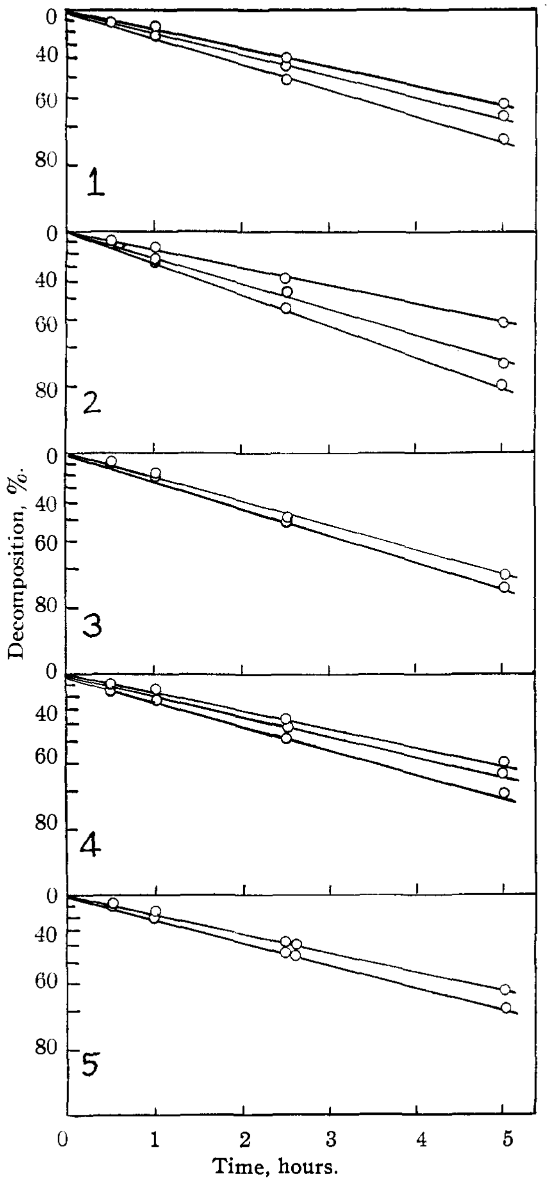
gram of solution. The results are summarized in Table I and plotted in Figs. 1–5 as percentage decomposition of benzoyl peroxide after heating at 80° for the indicated time interval.



Figs. 1–5.—The decomposition of benzoyl peroxide in polymerizing allyl esters at 80°: Fig. 1, allyl acetate; Fig. 2, allyl propionate; Fig. 3, allyl trimethylacetate; Fig. 4, allyl ethyl carbonate; Fig. 5, isopropenyl acetate. Data from Table I: upper curve, Bz_2O_2, 0.08 m./kg.; middle curve, Bz_2O_2, 0.2 m./kg.; lower curve, Bz_2O_2, 0.4 m./kg. The ordinate scale is proportional to log (100 − % decomposition).

TABLE I

THE DECOMPOSITION OF BENZOYL PEROXIDE IN ALLYL ESTERS AT 80 ± 0.1°

Ester	Initial peroxide concn., moles/kg.	Decomposition, % 1/2 hr.	1 hr.	2.5 hr.	5 hr.
Allyl acetate	0.0845	11.7	19.3	38.8	62.6
	.204	12.3	17.6	43.6	67.2
	.411	13.6	24.1	51.9	73.6
Allyl propionate	.0814	9.9	16.2	38.3	61.5
	.204	12.6	23.8	47.2	74.7
	.393	13.7	25.5	55.1	79.8
Allyl trimethylacetate	.0859	8.3	20.5	48.8	72.1
	.208	12.0	21.6	50.9	75.1
Allyl ethyl carbonate	.0836	8.1	15.4	37.5	60.1
	.204	9.3	21.6	41.7	64.3
	.370	13.5	23.8	48.7	71.4
Isopropenyl acetate	.0830	8.7	17.4	39.7	62.9
	.205	10.7	21.0	45.4	68.7

TABLE II

CONSTANTS IN THE DECOMPOSITION OF BENZOYL PEROXIDE IN POLYMERIZING ALLYL ESTERS AT 80 ± 0.1°

Ester	Initial wt. % peroxide	Peroxide, concn., mole/kg.	k_1, hr.$^{-1}$ (dec. Bz_2O_2)	dM/dP
Allyl acetate	2.05	0.0845	0.193	25.5
	4.94	.204	.223	20.8
	9.96	.411	.258	15.2
Allyl propionate	1.97	.0814	.191	22.2
	4.94	.204	.276	15.5
	9.52	.393	.320	12.3
Allyl trimethylacetate	2.08	.0859	.258	18.7
	5.05	.208	.281	15.7
Allyl ethyl carbonate	2.02	.0836	.184	27.7
	4.94	.204	.208	24.1
	8.96	.370	.245	14.5
Isopropenyl acetate	2.01	.0830	.200	25.1
	4.95	.205	.235	18.6

A plot as a first order reaction, from a common origin, of the per cent. decomposition of benzoyl peroxide in the allyl esters for a comparable initial catalyst concentration, as in Fig. 6, shows that the over-all rate of decomposition is greatest in allyl trimethylacetate. The constants for the over-all rate of decomposition are summarized in Table II.

The results indicate that in our series of allyl esters the order of the rate of decomposition is trimethylacetate > propionate > acetate > ethyl carbonate.

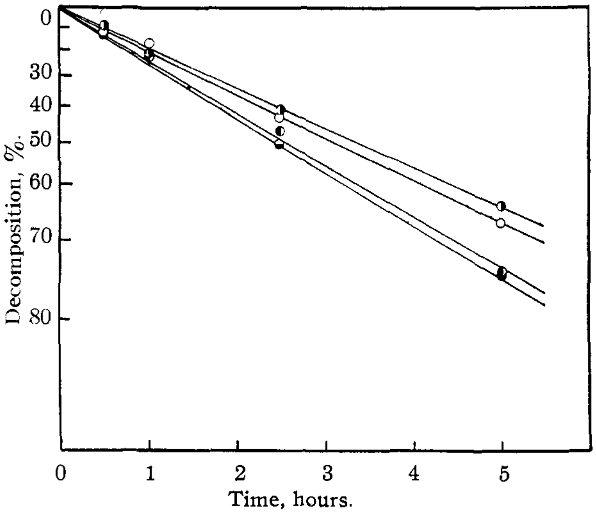


Fig. 6.—The decomposition of benzoyl peroxide in polymerizing allyl esters at 80°: ◑, P_0 = 0.204 m./kg. in allyl ethyl carbonate; ○, P_0 = 0.204 m./kg. in allyl acetate; ◐, P_0 = 0.204 m./kg. in allyl propionate; ◒, P_0 = 0.208 m./kg. in allyl trimethylacetate. The ordinate scale is proportional to log (100 − % decomposition).

It has been shown[10,11] that in the decomposition of benzoyl peroxide in aliphatic ethers the chain reaction involves attack upon hydrogen on the carbon alpha to the oxygen. In the case of the allyl esters hydrogen abstraction occurs on account of the predisposition of these compounds to form the allylic radical. A further activated position would be on the acidic portion of the ester involving the carbon adjacent to the carbonyl group. In alcohols it has been suggested[11] that in addition to attack upon the carbon alpha to the oxygen, a further mode of decomposition involves cleavage of the oxygen–hydrogen or of the oxygen–carbon bond

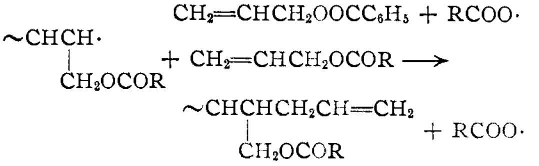
$$C_6H_5COO\cdot + RCH_2OH \longrightarrow C_6H_5COOH + R\underset{\cdot}{C}HOH$$

$$C_6H_5COO\cdot + RCH_2OH \longrightarrow C_6H_5COOH + RCH_2O\cdot$$

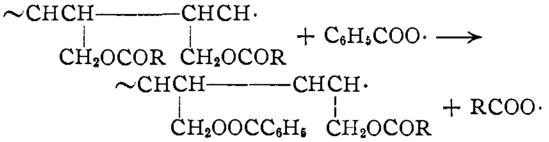
$$C_6H_5COO\cdot + RCH_2OH \longrightarrow C_6H_5COOCH_2R + \cdot OH$$

With reference to allyl esters, this would effect a free radical displacement reaction on the allylic carbon, as will be discussed more fully later.[12]

$$C_6H_5COO\cdot + CH_2{=}CHCH_2OCOR \longrightarrow CH_2{=}CHCH_2OOCC_6H_5 + RCOO\cdot \qquad (1)$$



$$\begin{array}{l}\sim CH\underset{\displaystyle CH_2OCOR}{\underset{|}{C}}H\cdot + CH_2{=}CHCH_2OCOR \longrightarrow \\ \qquad \sim CH\underset{\displaystyle CH_2OCOR}{\underset{|}{C}}HCH_2CH{=}CH_2 + RCOO\cdot\end{array} \qquad (2)$$



$$\begin{array}{l}\sim CH\underset{\displaystyle CH_2OCOR}{\underset{|}{C}}H{-}{-}{-}CH\underset{\displaystyle CH_2OCOR}{\underset{|}{C}}H\cdot + C_6H_5COO\cdot \longrightarrow \\ \qquad \sim CH\underset{\displaystyle CH_2OOCC_6H_5}{\underset{|}{C}}H{-}{-}{-}CH\underset{\displaystyle CH_2OCOR}{\underset{|}{C}}H\cdot + RCOO\cdot\end{array} \qquad (3)$$

This will result in the formation of an RCOO· radical which can decompose spontaneously to the alkyl radical and carbon dioxide or can liberate carbon dioxide at the moment of reaction with another molecule.[13,14]

$$RCOO\cdot + C_6H_5COO{-}OOCC_6H_5 \longrightarrow C_6H_5COOR + CO_2 + C_6H_5COO\cdot \qquad (4)$$

Reactions (1) to (3) provide an explanation for the sequence of decomposition rates, alternative to that by degradative transfer on the acyl group.

Arranging the free radicals in order of stability, *t*-butyl > ethyl > methyl > ethyloxy. It has been shown[5a] that decomposition of benzoyl peroxide is more rapid in the presence of hexaphenylethane than with pentaphenylethane. Thus the greater number of stable radicals from the former are more effective in inducing decomposition. Assuming the stability of a radical to be one of the decisive factors in its formation, the order of stability of the free radicals and consequently their rate of formation and the experimentally observed order of increased decomposition in the allyl esters agree. These alkyl radicals would arise from an intermediate radical, *e.g.*, the trimethylacetate radical for which this scheme appears particularly operative.

The variation in dM/dP[7] with initial benzoyl peroxide concentration in the allyl esters is shown in Table II. The order of dM/dP in the ester for comparable initial peroxide concentrations is the reverse of the order of the induced chain decomposition of peroxide, assuming that the latter is solely responsible for the variations in k_1 in the different monomers. However, the variations in dP/dt may be due to varying amounts of transfer with peroxide. This would confirm Bartlett's concept of chain decomposition,[5a] as wasting free radicals as far as initiating polymerization chains is concerned since peroxide molecules thus attacked yield a benzoate radical in place of the attacking radical and the other potential radical from the spontaneous unimolecular decomposition is lost. As indicated by Bartlett[5a,7] a further cause of the variation in dM/dP would be the wastage of chain initiators by mutual radical interaction prior to initiation of polymerization.

$$R\cdot + C_6H_5COO{-}OOCC_6H_5 \longrightarrow C_6H_5COOR + C_6H_5COO\cdot$$

Decomposition in Isopropenyl Acetate.—The similarity of the decomposition of peroxide in isopropenyl acetate to that in allyl acetate[15] is indicated in Tables I and II. This proves either that the isopropenyl and allyl groups are equivalent as regards stabilization of allylic resonance forms or that the decreased stabilization of the primary allylic type radical in isopropenyl acetate is balanced by the increased accessibility and decreased steric hindrance of the α-methyl group as compared to the α-methylene in allyl acetate.

Experimental

Materials.—Allyl acetate was prepared by refluxing allyl alcohol, acetic anhydride and glacial acetic acid in the presence of concentrated sulfuric acid. The ester was distilled twice, under nitrogen, through a 30 × 1.2-cm. air-jacketed column packed with $^1/_8''$ glass helices. The fraction, b.p. 53.2–54.0° (124 mm.), was collected.

Allyl propionate was prepared in a similar manner from allyl alcohol, propionic anhydride and propionic acid and had b.p. 123.5–124.0° (768 mm.).

Allyl ethyl carbonate was prepared by the dropwise addition of 559 g. (5.15 moles) of ethyl chloroformate to a mixture of 290 g. (5.0 moles) of allyl alcohol, 447 g. (5.45 moles) of pyridine and 750 ml. of absolute ether maintained below 10°. After filtration of pyridine hydrochloride the filtrate was washed with 25% hydrochloric acid followed by water-washes until neutral. After preliminary drying over calcium chloride the solution was dried over 20 g. of anhydrous potassium carbonate. The ester was distilled twice through the column described above and the middle fractions were collected, b.p. 143–144.5°, $n^{22.5}$D 1.4050.

Trimethylacetic acid was synthesized by the carbonation of the Grignard reagent from *t*-butyl chloride.[16]

Allyl trimethylacetate was prepared in two ways:

A. From Silver Trimethylacetate.—The silver salt was prepared in 80% yield from trimethylacetic acid, potassium hydroxide and silver nitrate by the method of Allen and Wilson.[17] The silver salt (84 g.) was refluxed for 10 hours, with stirring, with 150 ml. of allyl bromide. The precipitated silver bromide was filtered and the filtrate was distilled through a packed column. The fraction b.p. 135–140° was refractionated to give 26 g. of ester at 138–139° (45.6% yield based on silver salt, 36.6% based on acid).

B. From Pivalyl Chloride.—The acid chloride, b.p. 103–104°, was prepared in 94.6% yield from trimethylacetic acid and benzoyl chloride according to the method of Brown.[18]

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(10) W. E. Cass, THIS JOURNAL, **69**, 500 (1947).

(11) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(12) Part III of this series: *ibid.*, **74**, 337 (1952).

(13) P. D. Bartlett and R. Altschul, *ibid.*, **67**, 812 (1945).

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(15) N. G. Gaylord and F. R. Eirich, *J. Polymer Sci.*, **5**, 743 (1950).

(16) S. V. Puntambeker and E. A. Zoellner, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 524.

(17) C. F. H. Allen and C. V. Wilson, *Org. Syntheses*, **26**, 52 (1946).

(18) H. C. Brown, THIS JOURNAL, **60**, 1325 (1938).

The acid chloride, 279 g. (2.31 moles), was added dropwise to a mixture of 158 ml. (2.32 moles) of allyl alcohol, 371 ml. (4.6 moles) of pyridine and 500 ml. of toluene. The addition was completed in one hour and gentle reflux was maintained for an additional two hours. The reaction mixture was washed with 2 × 100 ml. water, 3 × 100 ml. 5% hydrochloric acid, 2 × 100 ml. 5% sodium hydroxide and again with 2 × 100 ml. water. After drying over 35 g. of calcium chloride and 15 g. of potassium carbonate, the ester was distilled under nitrogen. The product was collected at 138–140°, refractionated and collected at 138.5–138.7°, $n^{25}\mathrm{D}$ 1.4098. The yield was 155 g. (47.5% based on acid chloride, 44.6% based on acid).

Isopropenyl acetate from the Tennessee Eastman Co. was distilled and collected at 96–97°.

Benzoyl peroxide was purified by precipitation with methanol from chloroform solution and with distilled water from acetone solution.

Experimental Procedure.—A solution of benzoyl peroxide in the monomer was transferred by means of a hypodermic syringe to Pyrex tubes with constricted necks. The tubes were cooled in a Dry Ice–methanol-bath and evacuated on a Cenco–Hyvac oil-pump and then flushed with pure, dry nitrogen. Alternate evacuations and nitrogen flushings were repeated several times after which the tubes were sealed under vacuum. The tubes were suspended in a rocking wire basket in a constant temperature bath of paraffin oil maintained at 80 ± 0.1°. At measured intervals tubes were removed and dipped into the freezing mixture. The tubes were opened and samples were removed by hypodermic syringe for determination of peroxide concentration.

The concentration of benzoyl peroxide in the allyl esters was determined by iodometric titration in glacial acetic acid after addition of potassium iodide according to the method of Bartlett and Altschul.[7] The concentration of peroxide in isopropenyl acetate was determined by back titration of excess arsenious oxide with standard iodine according to the method of Siggia.[19]

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(19) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 102.

BROOKLYN, NEW YORK RECEIVED FEBRUARY 13, 1951

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Allyl Polymerization. III. Kinetics of Polymerization of Allyl Esters[1,2]

BY NORMAN G. GAYLORD[3] AND FREDERICK R. EIRICH

The peroxide-catalyzed bulk polymerization of allyl esters, attended by the phenomenon of degradative chain transfer, may also be accompanied, to a small extent, by secondary reactions, wherein hydrogen abstraction from the acid derived portion of the ester or a free radical displacement reaction occurs. The extent of these reactions determines the degree of further lowering of the $\overline{DP}$ beyond that brought about by the primary degradative attack. The following order of $\overline{DP}$ is found in the allyl esters: trimethylacetate < propionate < acetate < ethyl carbonate. A kinetic scheme is set up including these secondary reactions and the conditions under which it yields the experimentally observed constant dM/dP are discussed. The polymerization of isopropenyl acetate with benzoyl peroxide is almost identical with that of allyl acetate, the shift in the position of the ester group apparently producing little change in polymerization behavior. The reciprocal relation between $\overline{DP}$ and rate of Bz_2O_2 decomposition may be traced to a common cause, *i.e.*, the relative ease of transfer reactions on allylic molecules.

The benzoyl peroxide catalyzed bulk polymerization of allyl acetate at 80° yields a polymer with an average molecular weight of about 1300.[4] In any given polymerization, the concentration of monomer polymerized is, to a good approximation, a linear function of the concentration of peroxide decomposed, *i.e.*, dM/dP is constant. The constancy of dM/dP is attributed to degradative chain transfer[4] wherein active radicals, as in growing chains, yield stabilized radicals with lowered reactivity by abstraction of α-methylenic hydrogen from the allylic monomer. Emulsion polymerization of allyl acetate with potassium persulfate gives a polymer of the same average $\overline{DP}$ as in bulk polymerization indicating analogous initiation and termination mechanisms.[5]

In previous papers[6] it was shown that the decomposition of benzoyl peroxide in allyl alcohol, allyl bromide and several allyl esters was compatible with the existence of a spontaneous unimolecular reaction accompanied by a free radical induced chain decomposition. The present investigation is concerned with a study of the kinetics of the benzoyl peroxide catalyzed polymerization of allyl esters.

Experimental Results

The bulk polymerization of several allyl esters was carried out under vacuum at 80°, in the presence of varying initial concentrations of benzoyl peroxide. The concentrations of monomer and peroxide were followed as a function of time. Unsaturation and peroxide concentration were determined by the methods of Bartlett and Altschul.[4]

The results are summarized in Table I wherein the concentrations are expressed in moles per kilogram.[4] The constant value of dM/dP in a given run and the variation of this value with initial peroxide concentration are shown in Fig. 1.

Discussion

Secondary Degradative Attack.—As indicated by Bartlett and Altschul[4] there are two possible positions in allyl acetate from which hydrogen atoms might be removed to yield a free radical with greater stability than the attacking radical. Bartlett favored reaction 1 and rejected reaction 2 on the grounds that vinyl acetate which can undergo the second reaction but not the first, polymerizes to long chains with no appearance of degradative chain transfer, while allyl propyl

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(1) This work was carried out with the support of the U. S. Navy, Bureau of Aeronautics.

(2) Abstracted from a portion of the dissertation submitted by Norman G. Gaylord to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1950.

(3) E. I. du Pont de Nemours and Co., Yerkes Research Laboratory, Buffalo, N. Y.

(4) P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 816 (1945).

(5) P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

(6) N. G. Gaylord and F. R. Eirich; Part I, THIS JOURNAL, **73**, 4981 (1951); Part II, *ibid.*, **74**, 334 (1952).