and more of the copolymerization with oxygen, but the over-all rate of reaction of styrene does not change rapidly until the oxygen pressure drops to about 10 mm. Above this point the reaction of peroxide radicals with styrene (reaction 4) is rate-determining (among the propagation reactions). Below 10 mm. pressure, the life and concentration of styrene radicals increases more rapidly, and the concentration of peroxide radicals decreases. Reaction of unlike radicals becomes more important, and finally produces a sharp minimum in the rate of reaction of styrene below 1 mm. pressure. At 1 mm. pressure, where the concentration of oxygen is only about 7×10^{-6} *M*, the rates of reaction of styrene radicals with styrene, of styrene radicals with oxygen, and of peroxide radicals with styrene (reactions 2–4) become approximately equal.

As the oxygen pressure decreases, a maximum of 56% of the reacting oxygen appears as aldehydes at about 5 mm. pressure, and a maximum of 25% of the reacting oxygen appears as styrene oxide at 0.5–1.0 mm. pressure. For every molecule of epoxide formed, an ether link (or at least some irregularity) appears in the polymer (section 4.5). The declining yields of aldehydes and epoxide at pressures below the optima are due to the accumulation of excess monomer and irregularities in the polymer chains, which retard epoxide formation and depolymerization (section 4.6). As the oxygen pressure approaches zero, other products disappear and the polymer approaches polystyrene (Fig. 1). The rearrangement of $MO_2CH_2\dot{C}H(C_6H_5)$ radicals to MO· radicals and styrene oxide (reaction 8) is twice as fast as reaction with styrene solvent (section 4.6), the half-lives with respect to these reactions being about 0.4×10^{-3} and 10^{-3} second, respectively.

This study of the oxidation of styrene provided an unusual opportunity to study the effects of penultimate groups in copolymerization. As the concentration of oxygen decreases, the styrene radicals change from $MO_2M\cdot$ to $MM\cdot$. Most of this change takes place below 20 mm. pressure of oxygen, where the concentration of oxygen is less than 0.0002 *M*, or 0.002 mole %. In this region, the reactivity of styrene radicals both with oxygen (as measured by r_1, section 4.5) and with peroxide radicals (as measured by ϕ, section 4.1) increases at least 10-fold. Such steady concentrations of reactants would be difficult to attain with a more conventional monomer pair (*e.g.*, styrene and maleic anhydride), where similar relations presumably exist.

Finally, attention is called to some novel catalytic aspects of the autoxidation of styrene. In expt. 129, for example, at 15.3 mm. pressure, 58 molecules of styrene oxide and 239 molecules of benzaldehyde were formed per initiator molecule decomposed. If each decomposing initiator produced two radicals, then each radical produced a catalyst site or handle on which an average of 249 molecules of styrene and 218 molecules of oxygen added, in an almost alternating fashion. During this growth process, on 29 occasions, a terminal styrene radical split off styrene oxide, and each time about four molecules each of benzaldehyde and formaldehyde peeled off. More styrene and oxygen added to the residual radical and the process was repeated. The residual radical gradually increased in size as it accumulated ether links and peroxide units which were insulated from the active end of the radicals by excess styrene and ether units. Not all the growth took place on the original radical because the chain transfer process occasionally destroyed the activity of old residues and created new sites. We have, nevertheless, a homogeneous catalysis of oxidation which may be a model for some heterogeneous catalyses: several molecules of substrate have been oxidized on the same catalyst site. A more impressive case of the same type will be described in section 9.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY AND STANFORD RESEARCH INSTITUTE]

The Oxidation of Unsaturated Compounds. VI. The Effect of Oxygen Pressure on the Oxidation of α-Methylstyrene[1,*]

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The rates and products of oxidation of α-methylstyrene have been studied in the presence of 0.01 *M* ABN at oxygen pressures from 0–3200 mm. The primary products are a polymeric peroxide, acetophenone and formaldehyde, and α-methylstyrene oxide (β-phenylpropylene oxide). At 50°, the maximum yield of polyperoxide was 83% at 3200 mm. pressure of oxygen, of acetophenone, 70% at 50–100 mm., and of epoxide, 40% at 6 mm. The oxidation of α-methylstyrene differs from the oxidation of styrene in the following ways: (1) very little reaction of α-methylstyrene occurs in the absence of oxygen; (2) more cleavage of α-methylstyrene occurs at any pressure, and at least 15% even at high pressure; (3) high yields of volatile products with low conversions to polymeric residues are possible at low pressures. These results have been satisfactorily correlated with the mechanism proposed for styrene. Thermal and photodecompositions and reductions of the polyperoxide are described. α-Methylstyrene absorbs oxygen rapidly at 170° to give 33% acetophenone and formaldehyde, 38% epoxide and 29% of a low polymer. The solubilities of oxygen in several organic compounds have been measured.

6. Introduction

A study of the oxidation of α-methylstyrene, as well as of styrene, was of interest because the former monomer does not polymerize by a free radical mechanism in the absence of oxygen. The principal novel features of the oxidation of α-methylstyrene are summarized in section 9.

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* For numbering of footnotes, equations, etc., *cf.* note 2 of paper V.

7. Experimental

7.1. **Materials.**—α-Methylstyrene was obtained from Coleman and Bell, and from Eastman Kodak Co. It was fractionally distilled *in vacuo* and stored under nitrogen. Some monomer was also recovered from distillates and carefully fractionated to remove acetophenone and epoxide. α-Methylstyrene oxidized on storage, particularly when a storage bottle was opened several times. The increase in acetophenone was easily followed by the absorption of the 5.90 μ band, and the increase in epoxide seemed to be about half as great. In most experiments, the concentration of acetophenone in the initial monomer was at or below 0.05% by weight, 0.0037 mole/l. Low acetophenone content was essential in experiments carried out by procedure C, where conversions were low. Corrections have been entered for acetophenone (but not for epoxide) in some other experiments where more acetophenone was present and where the correction was relatively small, as indicated in Table VII. The other materials employed were like those noted in the previous paper.

The density of α-methylstyrene was taken as 0.882 g./ml. at 50°,[44] and the concentration of monomer in the pure liquid as 7.46 *M*.

7.2. **Procedures.**—The same three procedures, A, B and C, were used for oxidations and analyses as were described in section 2.2. The distillation temperature was about 15° higher than for styrene, but this difference was unimportant because α-methylstyrene does not polymerize in the absence of oxygen. Acetophenone was determined by infrared absorption at the 5.90 or 10.50 μ bands, depending on whether the acetophenone content was below or above 1%. Pure α-methylstyrene, prepared by fractional crystallization and distillation, has a weak absorption band at 5.90 μ, for which allowance was made in using standard reference curves. α-Methylstyrene oxide was determined from the band at 11.64 μ. These determinations were usually made on concentrates where the ketone and oxide had been concentrated 5–10 fold. The uncertainties in the total amounts of products formed are the same as for the corresponding products in the oxidation of styrene.

The following experiment illustrates an analysis of an old sample of α-methylstyrene: 7.51 g. of α-methylstyrene containing 0.25%, 0.019 g., of acetophenone was fractionally distilled at 46° and 10 mm. in the column used for procedure C; 7.40 g. of distillate containing 0.05% acetophenone, 0.004 g., and 0.11 g. of residue containing 10.8% acetophenone, 0.012 g. (and also 6.25%, 0.007 g., of α-methylstyrene oxide) were obtained. These results show that the column effects a reasonable separation of α-methylstyrene from acetophenone under extreme conditions, that the analyses for acetophenone provide a fair material balance under the same conditions, and that epoxide as well as acetophenone is formed on storage. Since the oxide boils higher than acetophenone, separation of oxide from monomer is not a problem.

7.3. **Rates and Products of Oxidation as Functions of Time.**—Experiment 81 shows that α-methylstyrene peroxide and acetophenone were formed concurrently, and how the rate of oxidation decreases with time. When 882 g. of α-methylstyrene, one liter at 50°, and 0.0100 mole ABN were stirred for 24.0 hours at 50° in a stream of oxygen at a total pressure of 746 mm., 72 g. of oxygen was absorbed. Samples were removed at intervals and analyzed for peroxide and acetophenone. The sample size varied from 10 to 1 ml. and was chosen to contain about 0.2 g. of peroxide. Analyses were carried out according to procedure C. The volatile material was analyzed, without concentration, by infrared. Most of the final product was also worked up by procedure A. Figure 8 shows that the ratio of acetophenone to peroxide is essentially constant and that both are primary products.[45] The data, part of which are in Fig. 8 and Table VII, show also that the rate of the ABN-initiated oxidation decreased regularly from 0.1066 mole/l./hr. during the first 7 hr. to about 0.091 during the last 1.7 hours, a decrease of about 14% for a 19% decrease in ABN concentration (from 3 to 23 hours). This initial rate corresponds to only about 600 mm. of oxygen in Fig. 9. Perhaps this large volume of solution was only 80% saturated with oxygen.

7.4. **Examination of Fractions.**—Experiment 127 provides the best data on the products of oxidation. α-Methylstyrene (878 g.) and 1.64 g. of ABN were stirred at 50° under a total pressure of 758 mm. for 24 hours. Oxygen was supplied at the rate of 0.644 mole/hr. The weight gain was 66.5 g. plus whatever formaldehyde was lost. Analysis of the products accounted for reaction of 2.367 moles of α-methylstyrene and 2.462 moles (78.8 g.) of oxygen. Of the monomer so found, 38.4% appeared as acetophenone (and, presumably, as 27.3 g. of formaldehyde), 0.9% as α-methylstyrene oxide, 60.0% as polyperoxide and 0.7% as an unidentified compound, $C_9H_{12}O_2$.

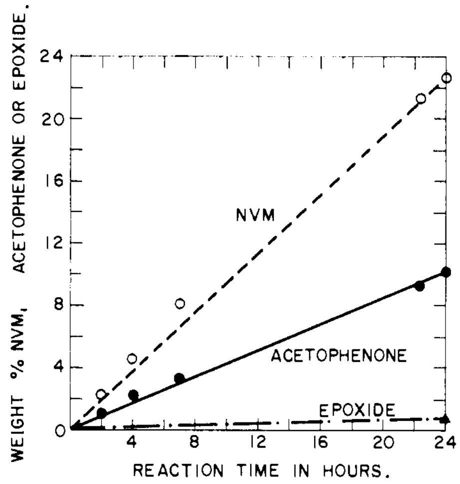

Fig. 8.—Oxidation of α-methylstyrene in expt. 81 (Table VII).

The final reaction mixture was analyzed by procedure A. After correction for all mechanical losses in sampling and transfer, 948.7 g. of final reaction mixture gave: (A) recovered and distilled α-methylstyrene containing 91.2 g. of acetophenone and 2.7 g. α-methylstyrene oxide; (B) 194.3 g. of methanol-insoluble peroxide, as a 73.5% solution in benzene; and (C) 46.1 g. of a methanol-soluble fraction, not volatile at 40° and 0.5 mm. pressure. Polymer B, when thoroughly freed of solvent, analyzed for 71.4, 71.2% C and 6.56, 6.66% H. The molecular weight, by freezing point in benzene, was 2114, 2093. This molecular weight is more likely to be too low than too high: if the sample contained 0.1% by weight of methanol, the molecular weight of the peroxide was 2250. Most of fraction C was warmed gradually, finally heated for one hour at 50–60°, at 0.1 mm. pressure, in a rotating molecular still. Investigation of the fractions showed that C consisted of 0.4% of α-methylstyrene, 39.6% of acetophenone, 3.8% of unidentified material of similar volatility (possibly mostly α-methylstyrene), 1.1% of ABN as crystals, 5.82% of an unidentified material D, 48.2% of non-volatile fraction E and 1.1% unaccounted for (partly paraformaldehyde). Fraction E was α-methylstyrene polyperoxide of low molecular weight. It analyzed for 66.9, 67.0% C; 6.79, 6.86% H; mol. wt., 632, 588. The nitrogen content of this fraction was negligible (<0.2%).

Although the material D seems to be only a minor by-product of the oxidation, an effort was made to identify it. The fraction from the molecular distillation which contained D was redistilled twice in a small flask at 0.7 mm. pressure. The boiling range narrowed to 70–80°. The final distillate contained 5% ABN and 6% acetophenone by infrared absorption, and analyzed for 71.6, 71.7% C; 7.94, 7.93% H. After correcting for known ABN and acetophenone, the analysis corresponds closely to $C_9H_{12}O_2$. Since D contains two hydrogen atoms and two oxygen atoms more than α-methylstyrene, a moloxide structure[46] is excluded. D analyzed for 0.96, 1.00% active hydrogen (Clark Microanalytical Laboratories), corresponding closer to two than to one active hydrogen in 89% $C_9H_{12}O_2$. The infrared absorption of D corresponds to a monosubstituted benzene, not to

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[44] Reference 7, p. 698.

[45] An identical conclusion was reached in a 8-hour experiment at 180 mm.

[46] H. Hock and M. Siebert, *Chem. Ber.*, **87**, 546 (1954).

a phenyl ether.[47] D is apparently a phenylpropane glycol, but (by infrared absorption) is neither 1,2-dihydroxy-2-phenylpropane (section 7.8) nor 1,3-dihydroxy-1-phenylpropane.[48] 1,3-Dihydroxy-2-phenylpropane[49] is a good possibility.

Polyperoxide fractions B and E were compared carefully to obtain information on end groups. The molecular weight of B was 3.5 times that of E; B contained 0.8% excess oxygen over that expected for $(C_9H_{10}O_2)_n$, E, 5.1% excess. Infrared spectra showed that E contained 4–5 times as much hydroxyl and carbonyl absorption as B. Comparison with benzyl alcohol suggested that there might be enough hydroxyl groups present in each fraction to account for one end group per molecule. There were two carbonyl absorption peaks in each sample, at 5.78 and 5.93 μ, corresponding to structures like those in α-phenylpropionaldehyde and acetophenone, respectively. The 5.78 μ aldehyde peak was 4–5 times as strong in E as in B. The 5.93 μ peak in E was only 1.7 times as strong as in B. Comparison with the indicated reference compounds showed that the combined carbonyl absorptions could account for about 0.6 end group per molecule. Absorption peaks at 9.3, 9.7 and 10.2 μ were about twice as strong in B as in E and are thought to be associated with C–O bonds not in terminal groups.

7.5. Preparation of α-Methylstyrene Polyperoxide.—Experiment 39 shows how a 13% conversion of methylstyrene to peroxide may be obtained quite simply: 883.8 g. of freshly distilled α-methylstyrene (1.001 l. at 50°) and 1.62 g. ABN (0.00988 mole) were stirred in a slow stream of oxygen for 24 hours at a bath temperature of 50° and a total pressure of 750 mm. The 921 g. of final reaction mixture (about 98.6% of that present if no samples had been removed) was poured into 2 l. of cold methanol to precipitate the polyperoxide. The polymer, after washing and precipitating according to procedure A, gave a benzene solution containing 143.2 g., 0.954 mole, of non-volatile methylstyrene peroxide analyzing for 71.4% carbon (theoretical for $C_9H_{10}O_2$, 71.98% C). The 921.4-g. final reaction mixture also contained (by infrared) 107 g. of acetophenone and 7–12 g. of α-methylstyrene oxide. These products, and the equivalent formaldehyde, account for 1.87 moles of oxygen, 59.8 g., in 921.4 g. of final reaction mixture. These proportions correspond to relatively more acetophenone and less peroxide than were found in expt. 81, but no attempt was made to recover the soluble peroxide in expt. 39.

7.6. Changes in Peroxide on Storage.—α-Methylstyrene peroxide decomposed slowly on storage to acetophenone and formaldehyde. A 73% solution in benzene showed no significant change in 3 months in a refrigerator 5°, but decomposed to the extent of about 5% in 206 days in the dark at room temperature. A 7.5% solution in chloroform at room temperature decomposed at the rate of about 1% in three weeks in the dark, 2–3% per day in diffused light. On storage, some minor changes occurred in infrared absorption of the polymers and their solutions, in addition to those due to accumulation of acetophenone: a general decrease at 10.2–11.1 μ, and increases at 8.85, 9.17, 10.0, 10.2 and 10.7 μ. These changes persisted in a polymer recovered from benzene solution by precipitation with methanol, but disappeared in a polymer recovered from chloroform solution. The changes may be associated with formation and polymerization of formaldehyde. Since the recovered polymers showed no significant difference in reduction (section 7.8), carbon analysis or carbonyl absorption, extensive rearrangement of the polyperoxide seems to be excluded.

7.7. Decompositions of α-Methylstyrene Peroxide.—Thermal and photodecompositions of α-methylstyrene peroxide in Table VIII were carried out with about 10% solutions of methanol-insoluble peroxide 127B in α-methylstyrene or benzene as solvent. The solutions were decomposed in sealed, evacuated tubes. Refluxing carbon tetrachloride or water was used to control temperature in most of the thermal experiments. Paraformaldehyde was usually recovered by filtration. A weighed portion of the reaction mixture was then distilled at about 0.5 mm. pressure up to a liquid temperature of about 60°. Acetophenone in the distillate was determined by infrared or with 2,4-dinitrophenylhydrazine (same procedure as for benzaldehyde[4]).

In some experiments, this first residue was investigated further. Acetophenone and α-methylstyrene (both present in only small quantities) were determined by infrared, and total oxygen in the residue by combustion for carbon and hydrogen. Most of this weighed residue was then heated slowly to 150–200° near 1 mm. pressure, or until material boiling much higher than acetophenone began to distil. This second residue was weighed and analyzed for carbon and hydrogen. Carbon and hydrogen analyses were run in duplicate and are averaged in Table VIII. All weights were corrected for mechanical losses.

Calculations are based on the following assumptions. The second residue contains oxygen only in carbonyl, ether or hydroxyl groups, the peroxide groups having been destroyed by strong heating. The first residue contains the oxygen of the second residue plus all the peroxide groups which had not been destroyed during previous heating or irradiation. After correction for small proportions of acetophenone and α-methylstyrene, the difference between the first and second residues corresponds to conversion of substantially all the peroxide oxygen in the first residue to acetophenone and formaldehyde. In expt. G, the material thus volatilized from the first residue corresponded to $C_9H_{13.6}O_{2.2}$, in expt. I, to $C_9H_{10.1}O_{1.79}$.

7.8. Reduction of α-Methylstyrene Polyperoxide.—This section shows that 50–60% yield of 1,2-dihydroxy-2-phenylpropane (identified by m.p. and infrared absorption in comparison with a known sample) may be obtained by catalytic reduction of polyperoxide or by reduction with hydrogen sulfide.

α-Methylstyrene peroxide (20.5 g.) in 59.5 g. of benzene and 60 g. of 96% ethanol was shaken with 1.00 g. of *t*-butylamine and 3.0 g. of modified Raney nickel catalyst[5] under 30–50 p.s.i. of hydrogen in a stainless steel bomb. The temperature rose spontaneously to 30°; then absorption of hydrogen nearly stopped; 3.0 g. more catalyst was then washed in with 5–10 ml. of ethanol and reduction was continued for 15.5 hours. The vessel was then heated for 8 hours at 50°. The product was filtered and distilled at reduced pressure, and the distillate was analyzed by infrared absorption.

The above procedure was employed on methanol-insoluble fractions of two peroxides, no. 81 which was 6 weeks old and no. 39 which had been stored for about a year at 7° and had shown some change in infrared absorption. Both absorbed the same amount of hydrogen, but the aged peroxide absorbed hydrogen faster (35% instead of 21% in the first period, 7% instead of 23% in the last period at 50°), gave a better yield of α-methylstyrene glycol (60% instead of 50%), and gave less α-phenethyl alcohol (14% instead of 28%). Peroxide 81 also gave 7% acetophenone, which may have come from decomposition, during distillation, of unreduced peroxide. Fresh no. 39 peroxide gave only 30% yield of glycol and some recovered peroxide in an early experiment when the hydrogenation mixture was not warmed above 35°. The α-phenethyl alcohol from reduction of no. 81 peroxide was identified both by its infrared spectrum and by the preparation of the acid phthalate.

Fresh no. 39 peroxide also gave 61% glycol by reduction with hydrogen sulfide. The only such reduction attempted was exploratory. Ten ml. of 0.5 *M* potassium hydrosulfide in 5 ml. of ethanol and 20 ml. of benzene was kept saturated and agitated by a stream of hydrogen sulfide. A solution of 10 g. of peroxide in 10 g. of benzene was added slowly without any noticeable temperature effect. Half was added over 6 hours while the bath temperature was increased to 50°; 5 ml. additional hydrosulfide was added, and then the remainder of the peroxide and another 5 ml. of hydrosulfide were added in 10 portions over 5 hours. After 2 more hours, the mixture was carbonated and distilled at reduced pressure to give 61% yield of glycol, 1.6% acetophenone, about 0.5% α-phenylpropionaldehyde and 14% of benzene-soluble higher-boiling material.

7.9. Oxidations Near 170°.—A few oxidations were carried out with refluxing α-methylstyrene under conditions like those employed for diisobutylene (paper VIII). These experiments were carried out with good stirring and with controlled heating with a Glas-Col mantle. In expt. 8T, substantially all of the oxygen in the air supplied was removed. In expts. 95 and 98, oxygen was supplied through

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[47] The assistance of Prof. Richard Eastman and of Dr. Peter Lim in this analysis is gratefully acknowledged.

[48] E. Fourneau, G. Benoit and R. Firmenich, *Bull. soc. chim.*, **47**, 860 (1930); M. G. J. Beets, *Rec. trav. chim.*, **70**, 20 (1951).

[49] According to H. Adkins and H. R. Billica, THIS JOURNAL, **70**, 3121 (1948), this glycol melts at 48.5–49°, consistent with the 27–29° found for our impure material.

a flowmeter. The boiling point depression due to gas flow was measured at the beginning and end of the oxidation and is a measure of the pressure of oxygen (formaldehyde and any other gases were neglected) above the stirred reaction mixture. The vapor pressure of α-methylstyrene changes 18 mm. for 1° change in temperature at 165°.

7.10. **Solubility of Oxygen.**—Solubilities of oxygen in some monomers and related solvents were measured by equilibrating oxygen in a gas buret with the degassed liquids, containing 0.1% quinone, at 25°. Corrections for the vapor pressures of the liquids were made using Henry's law. Table VI summarizes our results corrected to 760 mm.

TABLE VI

SOLUBILITIES OF OXYGEN IN MONOMERS AT 25°

Monomer or solvent	Solubility of oxygen at 760 mm. O_2, moles/l. × 10^3
Tetralin	7.6
Cumene	8.0
Styrene	7.1
α-Methylstyrene	6.4
Methyl methacrylate	10.6

pressure of oxygen. The solubilities in tetralin and styrene agree with determinations by Bateman, *et al.*,[50] and by Boardman and Selwood.[51] The data show only a small change in solubility of oxygen with monomer structure and with temperature.

8. Results and Discussion

8.1. **Effect of Oxygen Pressure on Rate of Oxidation.**—Data on the rate and products of oxidation of α-methylstyrene at 50° in the presence of 0.01 *M* ABN are summarized in Table VII[52] and Fig. 9. These data are based on the assumptions (to be considered in section 8.5) that the non-volatile product is entirely α-methylstyrene polyperoxide (except as noted for the first two listed experiments) and that formaldehyde equivalent to acetophenone was evolved from the reaction mixture. In the absence of oxygen, only 2.8 moles of α-methylstyrene reacted per molecule of ABN decomposed (in sealed, evacuated tube).[53] Therefore, the propagation reaction in which an α-methylstyrene radical adds to α-methylstyrene may be neglected ($k_p = 0$ in Tables III and IV), and peroxide radicals must be involved in propagation and termination reactions where appreciable monomer is consumed.

Figure 10 shows that in the pressure range 0–40 mm. of oxygen, the over-all rates of reaction of both α-methylstyrene and oxygen are proportional to the square root of the oxygen pressure. These relations correspond to a crossed chain termination by M· and MO_2· radicals (reaction 6 in Table III). At higher pressures, the rates of reaction increase slowly with oxygen pressure, but never become independent of oxygen pressure below 3200 mm. pressure of oxygen. Monomer radicals therefore contribute to chain termination, and are available for epoxidation and cleavage over this whole range.

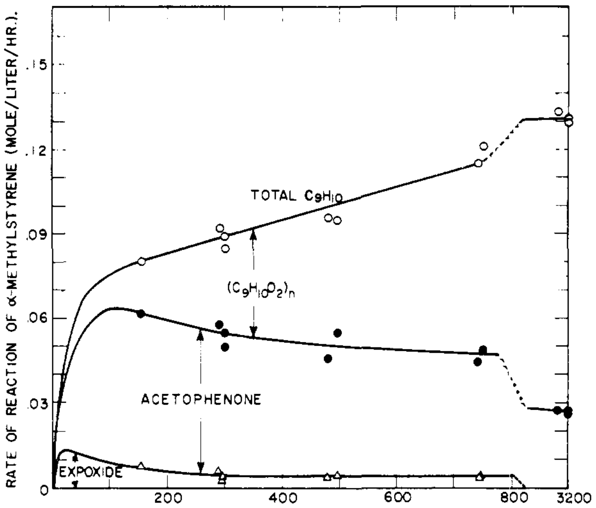

Fig. 9.—Rates and products of oxidation of α-methylstyrene in 6–7 hour experiments at 50° in presence of 0.01 *M* ABN. Experimental points at pressures below 150 mm. are in Fig. 11.

An unsuccessful effort was made to fit representative data to an equation like (19b)

$$R_O = \frac{[M][O_2]R_i^{1/2}/\xi_O}{([M]^2\xi_M^2/\xi^2_O + 2\phi[M][O_2]\xi_M/\xi_O + [O_2]^2)^{1/2}} \qquad (44)$$

where $\xi_M = (2k_{tm})^{1/2}/(k_{po} + k'_{ch} + k_{tr})$, $[M] = 7.46$ (section 7.1), and $[O_2] = 8.43 \times 10^{-6}p$ (section 7.10). The definition of ξ_M comes from equation 45 and section 8.4. Values of R_O were taken as 0.1301, 0.0861 and 0.0439 mole/l./hr. from averages, respectively, of 2 experiments at 3200 mm., 3 experiments at 290–301 mm., and 4 experiments at 24.5–25.3 mm. These results proved to be inconsistent with equation 44, for solution gave an imaginary value for ξ_M/ξ_O. The curve in Fig. 10 corresponds to equation 44 with $R_i^{1/2}/\xi_O = 0.0134$, with $2\phi\xi_M/\xi_O = 1.18 \times 10^{-4}$, and with the $[M]^2\xi^2_M/\xi^2_O$ term neglected. This curve fits the points at 25 and 297 mm., but gives 0.1000 as the high pressure limit of R_O, considerably below the experimental value at 3200 mm. A similar discrepancy was noted with styrene. These relations indicate that either initiation by ABN is less efficient at low oxygen pressures, or else that one of the quantities, ϕ, ξ_M or ξ_O, decreases as the oxygen pressure increases, and as the bonds to the penultimate units in M· change from ether and hydrocarbon links to peroxide links. The most reasonable of these changes are an increase in efficiency of initiation or an increase in k_{po} (reaction 3, M· + O_2) with increasing oxygen pressure.

No significant effect of stirring rate was found at 25 mm. pressure of oxygen and 0.01 *M* ABN (expts. 70–72 in Table VII). However, three kinds of evidence suggest that equilibrium concentrations of oxygen may not have been maintained at lower pressures or higher concentrations of initiator. (A) Rates of oxidation (R_O) for the 6 and 15 mm. runs in Fig. 10 are somewhat low, as judged by the theoretical curve through the 25 mm. points. (B) At 15 mm. pressure, the effect of a fourfold increase in catalyst concentration on the rate of reaction is relatively less than at 25 mm. (C) An increase in concentration of ABN increases the ratio of epoxide to acetophenone at either 15 mm. or 25 mm. of oxygen, corresponding to a decrease in the effective concentration.

The rate of reaction of α-methylstyrene is nearly proportional to $[ABN]^{1/2}$ at both extremes of the pressure range studied. Oxidation chains therefore terminate by a bimolecular reaction of two radicals. The observed exponents are actually 0.58 at 15 mm., 0.64 at 25 mm., 0.43 at 750 mm. and 0.59 at 3200 mm.

8.2. **Effect of Pressure on Products of Oxidation.**—The oxidation of α-methylstyrene gives polyperoxide, acetophenone and formaldehyde, and

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(50) L. Bateman, J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **47**, 280 (1951), found 0.0075 mole/l. in tetralin at 10°, 0.00775 at 65°.

(51) H. Boardman and P. W. Selwood, THIS JOURNAL, **72**, 1372 (1950), found 0.0057 mole/l. in styrene at 22°.

(52) Some difficulty was encountered in reproducing results with some lots of α-methylstyrene. Table VII does not include all α-methylstyrene data.

(53) G. Smets and L. DeHaes, *Bull. soc. chim. Belges*, **59**, 13 (1950), found that 15–22 molecules of α-methylstyrene polymerized per molecule of benzoyl peroxide decomposed at 85°. In view of the different temperatures and initiators employed, their results and ours are not necessarily inconsistent.

TABLE VII

THE AUTOXIDATION OF α-METHYLSTYRENE AT 50°

Expt.	Initial C_9H_{10}, g.	O_2 press., mm.	Moles O_2		Reaction time, hr.	Rates in moles/l./hr.[a]			
			Absorbed	Exhausted		$(C_9H_{10}O_2)_n$	AcC_6H_5[b] R_C	$C_9H_{10}O$ R_E	Total C_9H_{10} R_M
0.01 *M* ABN, no solvent									
133	129.0	0	0	0	68.0				0.00025[c]
93	176.6	5.9	0.025	0.16	6.55	0.0034[d,e]	0.0108	0.0096	.0240
120	132.4	15.0	.032	.61	7.00	.0052[e]	.0202	.0131	.0385
71	132.3	24.5	.040	.60	6.00[f]	.0075	.0308	.0137	.0520
70	132.2	24.6	.038	.54	6.00[f]	.0069	.0298	.0120	.0487
72	132.4	25.1	.038	.60	6.00[f]	.0066	.0298	.0134	.0498
61	132.6	25.3	.047	.77	7.00	.0063	.0314	.0141	.0518
78	132.4	49.7	.057	.20	6.15	.0085	.0465	.0115	.0665
65	133.1	75.1	.070	.76	7.00	.0121	.0487	.0112	.0720
97	132.5	101	.066	.43	6.08	.0139	.0530	.0092	.0761
76	132.4	154	.072	.67	6.30	.0189	.0537	.0074	.0800
96	132.6	290	.080	.86	6.00	.0342	.0515	.0058	.0915
60	132.5	300	.086	.47	7.00	.0351	.0456	.0040	.0847
75	132.4	301	.078	.42	6.00	.0335[g]	.0519	.0032	.0886
77	132.4	479	.083		6.00	.0499	.0416	.0039	.0954
63	132.5	496	.097	2.48	7.00	.0400	.0503	.0043	.0946
74	132.0	743	.101	0.6	6.00	.0709[g]	.0404	.0037	.1150
86	132.2	750	.099	.50	6.00	.0719	.0446	.004	.1206
81	882	736[h]			7.00	.0685	.0355	.0026[l]	.1066[h]
			2.31		24.00	.0620	.0312	.0023	.0955[h]
127	878	745	2.46	13.1	24.00	.0589[j]	.0377	.0009	.0982[h,i]
Co 7	9.06	3160		0	1.05	.1003	.0224	0	.1227
116	9.06	3200		0	1.00	.1030	.0264	0	.1294
121	9.06	3180		0	1.00	.1060	.0274	0	.1334
122	9.06	3200		0	1.00	.1041	.0268	0	.1309
117	4.53[k]	3160		0	2.30	.0450	.0126	0	.0576
123	4.53[k]	3110		0	2.00	.0476	.0100	0	.0586
0.002 *M* ABN in 125–126, 0.04 *M* ABN in 62, 66 and 79, 0.0667 *M* in 134									
79	132.4	15.1	0.039	0.14	4.03	0.0149[g]	0.0361	0.0285	.0795
62	132.7	25.0	.105	.49	7.00	.0147	.0653	.0394	.1194
66	132.8	24.9	.047	.24	3.00	.0160	.0713	.0356	.1229
125	9.06	3200		0	2.00	.0413	.0094	0	.0507
126	9.06	3190		0	2.65	.0434	.0089	0	.0523
134	132.4	753	.27	0.29	7.00	.1565	.1015	.013	.271
No ABN									
94	176.4	740	0.064	0.48	24.00	0.0086	0.0050	0.0006	0.0142
118	18.12	3230		0	7.00	.0024	.0005	0	.0029

[a] Average rates over whole reaction period. [b] Rates of formation of acetophenone have been corrected for acetophenone present in the original reaction mixture as follows: expt. 93, 0.0003 mole/l./hr.; 96 and 97, 0.0008; 108, 0.0060; 84, 0.0024; 100, 0.0023; 101, 0.0020; 114, 0.0011. [c] 128.4 g. of reaction mixture was concentrated up to 140° at 1 mm. pressure to remove monomer and initiator; 0.28 g. of oil containing 2.07% N remained. In the calculations each N atom is assumed to be associated with a terminal $(CH_3)_2C(CN)-$ group and the α-methylstyrene reacted is multiplied by 1.16 to allow for depletion of ABN.[9] [d] Excess C_9H_{10} was incorporated at rate of 0.0002 mole/l./hr. [e] *Cf.* Table X. [f] Expts. 70, 71, 72 were stirred at 1800, 1200 and 1500 r.p.m. respectively. [g] Peroxides 74, 75 and 79 had carbon contents ranging from 71.8 to 72.2%, indistinguishable from the theoretical 71.98%. [h] The low rate suggests that the large volume of solution was not saturated with oxygen. [i] Includes formation of unidentified $C_9H_{12}O_2$ at rate of 0.0007 mole/l./hr. Details in section 7.4. [j] Analyses in section 7.4. [k] Equal volume of benzene present. [l] Estimated.

α-methylstyrene oxide as primary reaction products. The cleavage products are also decomposition products of the polyperoxide, but Fig. 8 and section 7.3 demonstrate that the acetophenone formed in the oxidation of α-methylstyrene does not arise from decomposition of the polyperoxide. Comparison of 6- and 24-hour runs at 1 atm. of oxygen in Table VII shows that the epoxide is also a primary product. Figures 9 and 11 show how the primary products of oxidation of α-methylstyrene vary with oxygen pressure. Figure 9 covers the entire pressure range and shows monomer distribution among the products. Figure 11 covers only the low pressure range and shows how the rate of formation of each individual product varies with pressure. All the experimental points in Table VII with 0.01 *M* ABN in runs of 7 hours or less, except Co 7, appear in either Fig. 9 or Fig. 11

The oxidation of α-methylstyrene resembles that of styrene but exhibits some important differences: (A) The absence of homopolymerization of α-methylstyrene practically eliminates excess monomer from the polymer and reduces irregularities in the peroxide radical. (B) The yields of polymer at low pressures are so low that extensive decomposition of terminal alkoxy radicals must occur (reactions 9a and 9b). (C) Although some properties of the polyperoxide produced change markedly as

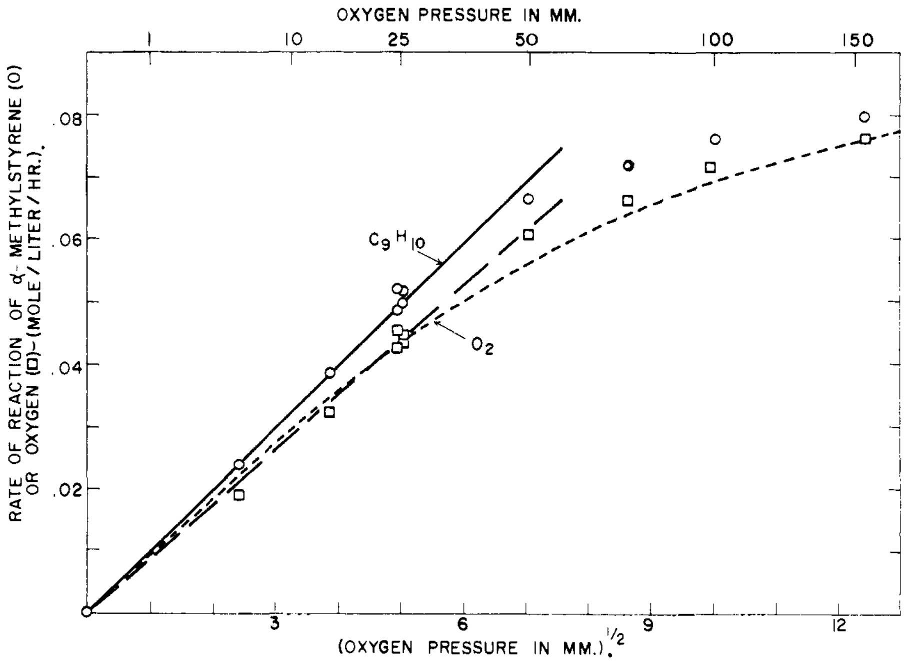


Fig. 10.—Rates of reaction of α-methylstyrene and oxygen in presence of 0.01 *M* ABN at 50°.

the oxygen pressure is reduced, the proportions of carbon, hydrogen and oxygen in the polymer do not. This situation increases the difficulty of a quantitative treatment. (D) Considerable cleavage of α-methylstyrene persists even at high oxygen pressures.

The decomposition of α-methylstyrene, in section 8.3, shows clearly that depolymerization of alkoxy radicals from the polyperoxide is rapid and nearly complete, even in α-methylstyrene (a good radical trap) as solvent. Section 8.4 will then show that data on the formation of epoxide and cleavage products are consistent with reactions 8–12. The structure of polyperoxides made at both high and low oxygen pressures will be considered in section 8.5. Sections 8.6 and 8.7 are concerned with thermal oxidations of α-methylstyrene at 50 and 170°.

8.3. Thermal and Photodecompositions of α-Methylstyrene Peroxide.—Hock and Siebert[46] showed that α-methylstyrene polyperoxide decomposes into acetophenone and formaldehyde by the action of heat or light. The corresponding decompositions of styrene polyperoxide have been studied in some detail and found to be chain reactions complicated both by the benzaldehyde formed[5] and by a non-chain decomposition (section 4.4). This section will present first some studies of rates and quantum yields in the photolysis of α-methylstyrene peroxide, then some product studies on both the thermal and photodecompositions in α-methylstyrene as solvent. These decompositions have been relatively simple to carry out and interpret, partly because acetophenone is relatively inert, and partly because α-methylstyrene is a good radical trap (with a reactive double bond[16]) without being susceptible to polymerization by free radicals. These decompositions establish clearly that the depolymerization mechanism for cleavage (reaction 9) can be rapid and complete.

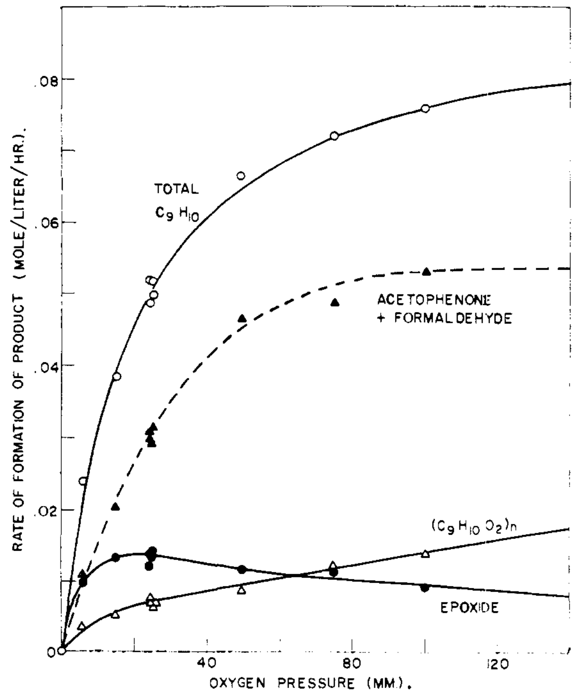


Fig. 11.—Rates of products of oxidation of α-methylstyrene at 50° in presence of 0.01 *M* ABN.

The first photodecompositions to be discussed employed the same apparatus and techniques used in the quantitative studies of styrene peroxide.[5] The quantum yields and effects of retarders leave no doubt as to the chain nature of the photolysis. Rates were determined by analysis of solutions for acetophenone with 2,4-dinitrophenylhydrazine. No other products were sought. With an A-H4 mercury lamp, Pyrex filter and a 0.5 *M* solution of peroxide in benzene, 42% of the peroxide was converted to acetophenone in two hours at 27°, and 21 molecules of this ketone were produced per quantum absorbed.

Figure 12 shows that the photolysis is only $^1/_6$ to $^1/_8$ as fast in α-methylstyrene as solvent as in benzene. To determine whether the effect might be due to a filtering of radiation by the monomer, 0.5 *M* solutions of the peroxide in benzene were surrounded by pure benzene or α-methylstyrene as filters. The closely similar rates with the two different filtering solutions in Fig. 12 show that the retarding effect of α-methylstyrene as solvent is due to its ability to trap radicals in the photolysis chain, not to its absorbance of light.

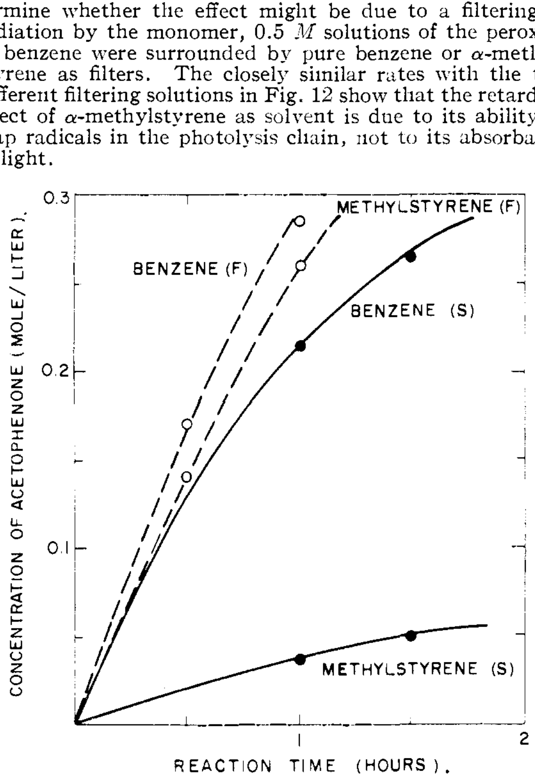


Fig. 12.—Photolysis at 30° of 0.5 *M* α-methylstyrene polyperoxide in benzene or α-methylstyrene as solvent (S), or in benzene solution with these solvents as filters (F).

Hydroquinone, oxygen and thiophenol also retard the photolysis of α-methylstyrene peroxide. With 0.4 *M* hydroquinone and 0.4 *M* peroxide (as $C_9H_{10}O_2$ units) in benzene at 25–30°, the rate of formation of acetophenone was only 12% of the control rate. Hydroquinone is probably converted to quinone, since a yellow color developed when the reagent and peroxide were irradiated together, but not separately. With 0.5 *M* peroxide in benzene at 25–30°, the rate of photolysis in a slow stream of oxygen was 40–50% of the rate in a similar stream of nitrogen. In contrast to these retarders, thiophenol seemed to be a better retarder at later stages of the photolysis, as shown in Fig. 13. Since the photodecomposition of styrene peroxide is not retarded by thiophenol,[5] it may be inferred that a $C_6H_5S\cdot$ radical may remove a benzyl hydrogen atom from styrene peroxide (not available in methylstyrene peroxide) to continue reaction chains.

Figure 13 indicates also that the effect of temperature on the photolysis of α-methylstyrene peroxide is small.

Table VIII summarizes thermal and photochemical decompositions of α-methylstyrene peroxide carried out with no. 127 peroxide as described in section 7.7. The products were essentially acetophenone, formaldehyde and a high-boiling, nearly colorless residue approximating $(C_9H_{10}O)_n$. Formaldehyde was not determined but always appeared both as gas and white solid, in quantities which are assumed to be equivalent to acetophenone. The 105.5% oxygen accounted for in expt. J may be due to incorporation of some formaldehyde in the residue. No important proportion of α-methylstyrene oxide (see Table VIII) or of any other volatile product was found.

The important points in Table VIII are the following. More than 80% of the oxygen in the peroxide decomposed appears as acetophenone and formaldehyde, the remainder as ether or hydroxyl groups in the residue. In α-methylstyrene as solvent, the decomposition is approximately first order in α-methylstyrene peroxide with an indicated activation energy (expts. C and D) of 35 kcal./mole. The yield of acetophenone/(acetophenone plus non-peroxide residue) increases regularly from 81 to 93% as the decomposition temperature increases from 50 to 150° (expts. J, G, E and K). Although the yield of acetophenone is the same in benzene and α-methylstyrene as solvents at 77°, the rate of decomposition is 2–4 times as fast in benzene.

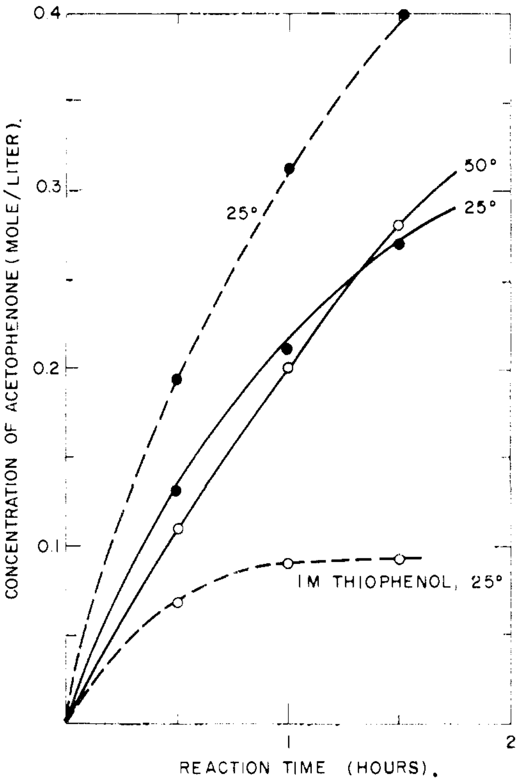


Fig. 13.—Photolysis of 0.5 *M* α-methylstyrene polyperoxide in benzene solution, with and without added thiophenol. Curves with solid lines are not comparable to curves with broken lines because of slightly different arrangements of apparatus.

The conclusions from Table VIII may now be combined with the photochemical data previously presented to give a more detailed picture of the decomposition of α-methylstyrene peroxide. Thermal rupture of a peroxide bond requires an activation energy of about 35 kcal./mole. Since the rate of photodecomposition is nearly independent of temperature, subsequent depolymerization of the alkoxy radicals requires little or no activation energy. Three kinds of evidence suggest that this depolymerization of the alkoxy radicals is nearly complete, leaving only the terminal radicals. (A) The peroxide employed had a number average molecular weight of 2400, and averaged $(C_9H_{10}O_2)_{16}$. Of the sixteen O_2 units available per molecule, 13–15 participated in depolymerization over the range 50–150°, leaving only 1–3 associated with the two terminal radicals, with side reactions, or with irregularities in the polyperoxide. (B) At 77° the yield of acetophenone was the same in α-methylstyrene as in benzene solution. This result is consistent with the lower rate in α-methylstyrene only if depolymerization was complete in both solvents and if α-methylstyrene served only to retard extension of the depolymerization to other molecules of peroxide. (C) On this basis, the slightly increased yield of acetophenone at higher tempera-

TABLE VIII

DECOMPOSITIONS OF α-METHYLSTYRENE PEROXIDE

Expt.	$(C_9H_{10}O_2)_n$, g.	Wt. % peroxide in C_9H_{10} solution	Reaction Time, hr.	Reaction Temp., °C.	Original oxygen, %, appearing as Ac–C_6H_5[a]	Epoxide	Undec. $C_9H_{10}O_2$	Non-peroxide residue	k_1,[b] hr.$^{-1}$
A. Thermal decompositions in α-methylstyrene									
B	1.30	8.73	24.2	77	53	0.2			0.037
C	1.19	8.73	72	77	76	1.0			.025
G	11.1	9.88	96	77	81	<0.2	5.6	12.0[c]	.028
D	1.16	8.73	3.0	100	76				.60
E	1.12	8.73	24	100	93	<0.2		9.5[d]	
K	5.86	10.0	~1 hr.[e]	145–155	93.2	~1	0	5.2[e]	
B. Thermal decompositions in benzene									
L	1.09	10.0	2.0	77	12.6				0.079
M	1.12	10.0	6.0	77	32.6				.11
N	6.79	10.0	96	77	82.6	<0.2		15.0[f]	
C. Photodecompositions in α-methylstyrene; sunlight[g]									
A	0.87	8.73	15	~25	78	0.2			
J	8.89	10.0	71.5	45–50	81.8		4.1	19.6	0.05

[a] Assuming formation of equivalent formaldehyde. [b] Apparent first-order rate constant based on ultimate yield of 85, 87 and 91% acetophenone at 50°, 77° and 100°. [c] 82.1% C, 7.85% H, corresponding to $C_9H_{10.3}O_{0.85}$. [d] 82.6% C, 7.85% H, corresponding to $C_9H_{10.2}O_{0.73}$, includes any peroxide not decomposed. [e] About 5% of the solution was heated quickly to 150° over a free flame under a slow stream of nitrogen. The remainder of the solution was added dropwise during 80 min. Non-volatile product analyzed for 84.25% C, 8.26% H, corresponding to $C_9H_{10.53}O_{0.60}$. [f] Includes water found when residue was heated to 150° at 20 mm. pressure. Additional water may have been lost. [g] Reaction times are for exposure to sunlight for about 3 days in August (A), or 35 days including December (J). Experiment A was stored near 0° between exposures, J near room temperature.

TABLE IX

LIMITING RELATIONS AMONG RATES OF EPOXIDATION, CLEAVAGE AND TOTAL OXIDATION

High pressures	Low pressures	
$\frac{R_E}{R_O} = \frac{k_e}{8.4 \times 10^{-6} p k_{po}} = \frac{20\ (\pm 2)}{p}$	$\frac{R_E}{R_O} = \frac{1}{1 + 0.09p}$	(1)[a]
$k_e/k_{po} = 0.00017$	$k_e/k_{po} = 0.00009$	
$\frac{R_C}{R_O} = \frac{k'_{ch}[M\cdot][O_2]}{R_O} + \frac{nR_E}{2R_O} = 0.14 + \frac{10n}{p}$	$\frac{R_C}{R_E} = \frac{0.07p + 0.5}{0.09p + 1}$	(0.5)[a]
$n = (k_{po} + k_{tr})/k_{tr} = 21.5$, or		
$n = \frac{k_{po}[M\cdot][O_2]/R_O + k_{tr}[M\cdot][O_2]/R_O}{k_{tr}[M\cdot][O_2]/R_O + R_E/R_O}$		
$n = \frac{0.82 + 0.04}{0.04 + 20/p} = \frac{21.5p}{p + 500}$		
$R_C/R_E = 0.007p + n/2$	$R_C/R_E = 0.07p + 0.5$	(0.5)[a]

[a] Limiting value of ratio at zero pressure.

tures is due to more complete decomposition of terminal radicals (reactions 9a and 9b).

These conclusions lead to others about quantum efficiencies and kinetic chain lengths at 25–30°. The quantum yield of acetophenone from α-methylstyrene peroxide in benzene solution at 25° is 21. In the presence of equivalent hydroquinone or of α-methylstyrene as solvent, the rate of photodecomposition is reduced by a factor of 6–8. Nevertheless, depolymerization of each polyperoxide molecule in the presence of retarders is essentially complete, as indicated by the production of 12–13 molecules of acetophenone from a peroxide molecule of 16 units (expt. A in Table VIII). Therefore, about 80 molecules of acetophenone are produced per initial chain cleavage in benzene solution, and only about one quantum in four absorbed is effective in initiating depolymerization of peroxide in benzene. The decomposition of at least 5–7 other molecules of peroxide is induced (in the absence of retarder) by the terminal radicals from photolysis of the first molecule.

8.4. Epoxidation and Cleavage.—While epoxidation and cleavage in the oxidation of α-methylstyrene proceed by the same reactions 8 and 9 as with styrene, they differ in detail. Extensive decomposition of terminal alkoxy radicals (reactions 9a and 9b) and repeated depolymerization to the same chain ending impose restrictions on the low pressure reactions. Differences between the high-pressure and low-pressure reactions are compared in Table IX.

The high pressure reactions will be considered first. A quantitative treatment requires some assumptions, implied in equation 45.

$$R_O = k_{po}[M\cdot][O_2] + k'_{ch}[M\cdot][O_2] + k_{tr}[M\cdot][O_2] \quad (45)$$

For reasons indicated in section 5 and just below, reactions 41 and 42 are assumed to regulate molecular weight, and reaction 12, rather than 11, is assumed to account for high-pressure cleavage. It is further assumed that each depolymerization results in the formation of an HO· radical, which reacts only with monomer. Therefore R_O in any experiment is $R_M - R_E$ from Table VII. The consequences of making these choices, instead of their alternatives, are not important for present purposes.

The first quantity of interest is the limiting value of R_E/R_O, proportional to $1/p$ at high pressures. Figure 14 shows R_E/R_O as a function of $1/p$, but it is clear that errors in the determination of small proportions of epoxide are serious, and that the line defined by the solid circles curves at low pressures. More reliance can be placed on low-pressure points if we allow for the fact that only R_O/R_M of the monomer radicals are capable of giving epoxide. If we plot $R_E R_M/R_O^2$ against $1/p$, the limiting slopes of this curve (open circles) and the R_E/R_O curve are the same, about 20.

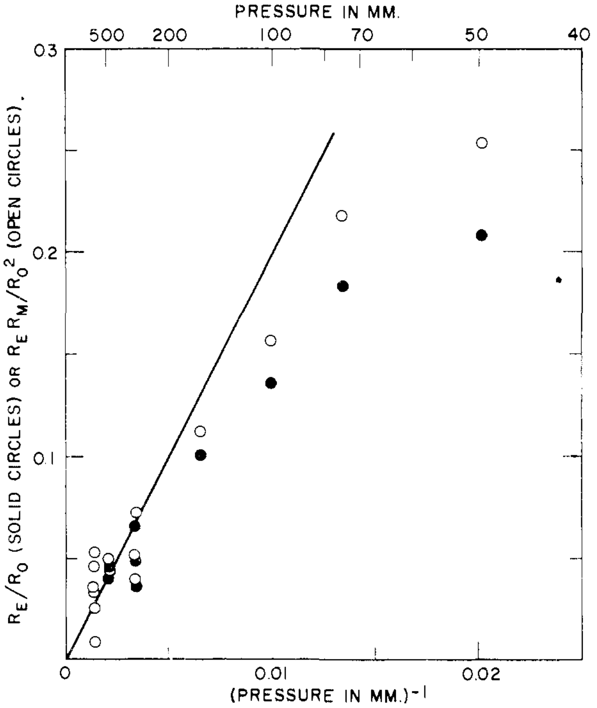


Fig. 14.—Relative rates of epoxidation (R_E) and total oxidation (R_O) as a function of oxygen pressure in the oxidation of α-methylstyrene at 50°. Calculations correspond to high-pressure relations in Table IX.

The next point of interest is R_C/R_O as a function of pressure. Figure 15 and Table VII indicate that some cleavage persists at 4 atmospheres of oxygen and that here R_C/R_O is nearly independent of the concentrations of oxygen, monomer and ABN. This cleavage must therefore involve the same reactants as one of the chain propagation reactions 11 or 12. The latter has been chosen as a basis for discussion because it is associated with the faster and more exothermic propagation reaction. The rate of pressure-dependent cleavage should be equal to the rate of epoxide formation times $n/2$, where n is the average number of $-O_2M-$ units between interruptions of this sequence in the polyperoxide being formed. If we neglect the contribution of epoxide formation to interruptions, then $n = 21.5$, from equation 45 and the relations in Table IX: $k'_{ch}[M\cdot][O_2]/R_O = 0.14$, $k_{tr}[M\cdot][O_2]/R_O = 0.04$ section 8.5, and k_{po} $[M\cdot][O_2]/R_O = 0.82$ (by difference). However, epoxide formation also interrupts the $-O_2M-$ sequence because all the monomer and oxygen which reacted since the previous interruption are no longer available for cleavage. Accordingly, an alternative value for n is given in Table IX. The two curves in Fig. 15 correspond to two sets of values for R_E/R_O, based on two sets of values for n, and on $R_E/R_O = 20/p$. The curves show that at high pressures, the principal factor limiting n is the length of the growing radical, which depends on a chain transfer reaction. As the pressure is reduced, the proportion of cleavage is limited by some other factor, presumably the unavailability of $-O_2M-$ units already lost in depolymerization, but the correction suggested is too large. In any event, the relative positions of the experimental points and the limiting calculated curves strongly support the general scheme proposed.

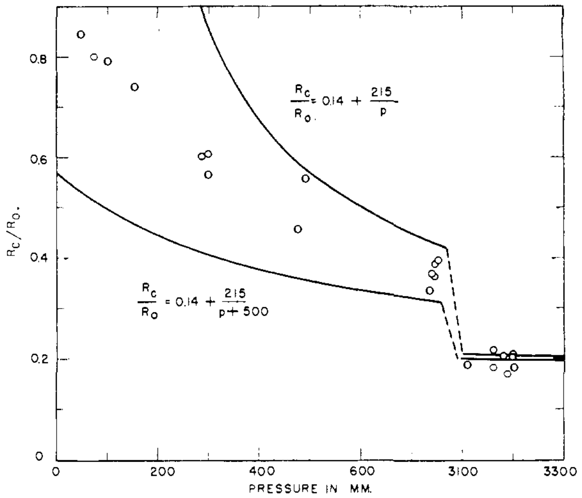
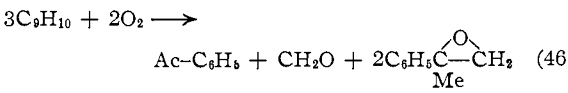


Fig. 15.—Relative rates of cleavage (R_C) and total oxidation (R_O) as a function of oxygen pressure in the oxidation of α-methylstyrene at 50°. Calculations correspond to high-pressure relations in Table IX.

Figure 16 plots R_C/R_E as a function of oxygen pressure. The two upper curves are calculated from R_E/R_O and the two values for R_C/R_O in Table IX. The lowest line in Fig. 16 represents cleavage by the high pressure mechanism. The difference between this line and either of the upper curves is $n/2$, the potential depolymerization of an average monomer radical. These curves are of decreasing significance below 200 mm. of oxygen.

The low pressure limits of the above relations are less certain, but a good case can be made for those chosen for Table IX. These limits follow from the postulate that the limiting over-all reaction at low pressures is

 (46)

$$3C_9H_{10} + 2O_2 \longrightarrow Ac\text{-}C_6H_5 + CH_2O + 2C_6H_5\underset{Me}{C}\overset{O}{\frown}CH_2 \quad (46)$$

This postulate will now be justified. The polymers produced in oxidations at 5–50 mm. pressure contained only 12–13% of the total monomer reacted, and only 0.37–0.74 mole of monomer per mole of epoxide formed (and per depolymerization chain). Since around 50% of this monomer was

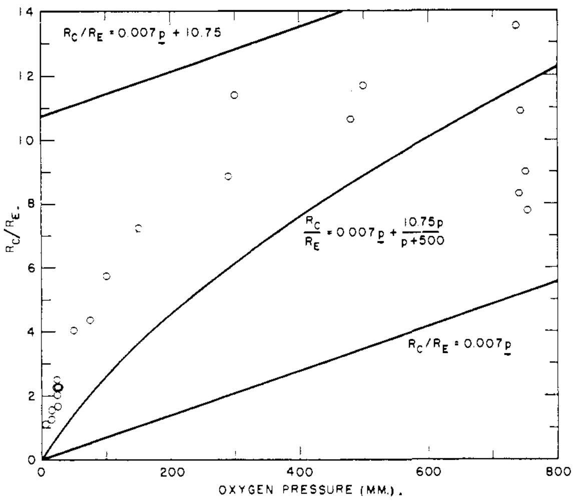


Fig. 16.—Relative rates of cleavage (R_C) and epoxidation (R_E) as a function of oxygen pressure in the oxidation of α-methylstyrene at 50°. Calculations correspond to high-pressure relations in Table IX.

polyperoxide which escaped decomposition, this amount of residue is far too little to allow for *any regular* accumulation of residue accompanying either epoxidation or cleavage. Accordingly, both reactions 9a and 9b must usually follow 9 with α-methylstyrene at low pressures. These considerations will be modified and refined in the next section. The above restrictions suggest the following sequence for the limiting ideal reaction at very low pressures, the net result being reaction 46.

$$
\begin{array}{rcll}
R''\cdot + O_2 & \longrightarrow & R''O_2\cdot & (1b) \\
R''O_2\cdot + M & \longrightarrow & R''O_2M\cdot & (4) \\
R''O_2M\cdot & \longrightarrow & R''O\cdot + \text{epoxide} & (8) \\
R''O\cdot + M & \longrightarrow & R''OM\cdot & (10) \\
R''OM\cdot + O_2 & \longrightarrow & R''OMO_2\cdot & (3) \\
R''OMO_2\cdot + M & \longrightarrow & R''OMO_2M\cdot & (4) \\
R''OMO_2M\cdot & \longrightarrow & R''\cdot + CH_2O + \text{Ac-}C_6H_5 + & \\
 & & \text{epoxide} & (8 + 9a + 9b)
\end{array}
$$

These reactions are special cases of the indicated numbered reactions. In this ideal sequence, R·″ is a free radical which can be used repeatedly to oxidize relatively large proportions of α-methylstyrene to α-methylstyrene oxide, acetophenone and formaldehyde. In practice, R·″ accumulates some monomer, monomer fragments and ether and peroxide links, as presented in section 8.5. Additional cleavage products and stable peroxide result as the oxygen pressure is increased. The essential and reasonable features of the ideal sequence are that R″OM· and peroxide radicals ($MO_2\cdot$) are stable while $R''O_2M\cdot$ and R″OMO· radicals decompose promptly at low oxygen pressures. The nature and efficiency of R·″ and the composition of the accumulated residues will be considered in sections 8.5 and 9.

This ideal cyclic process can be used to calculate the ratios in Table IX at low pressures. For these calculations $R_O = R_M - R_E/2$, from Table VII. This relation applies when depolymerizations to the same radical ending occur an even or large number of times, while $R_O = R_M - R_E$ applies for one depolymerization to the same radical ending. The ratio k_e/k_{po} is considered first. Of the radicals in the ideal cyclic process which can add oxygen, only those which have a penultimate O_2 unit are capable of giving epoxide. Therefore

$$\frac{R_E}{R_O} = \frac{k_e[M\cdot]}{k_{po}[M\cdot][O_2]} \times \frac{k_{po}[O_2]}{k_e + k_{po}[O_2]} = \frac{k_e}{k_e + 8.4 \times 10^{-6}\,pk_{po}} = \frac{1}{1 + 0.09p} \quad (47)$$

where the $k_{po}[O_2]/(k_e + k_{po}[O_2])$ factor is the fraction of monomer radicals capable of giving epoxide. The lowest curve in Fig. 17 corresponds to equation 47 and is based on the 15 mm. and 25 mm. points, which check very well. Table IX compares k_e/k_{po} for radicals in the cyclic and long chain sequences. The short radicals are either relatively less reactive in epoxidation or more reactive in propagation than the $M(O_2M)_m\cdot$ radicals where *m* is larger. The R_C/R_E curve in Fig. 17 is based on the 25 mm. points and the assumed intercept. Presumably $R_C/R_E = n/2$. The R_C/R_O curve is based on the R_E/R_O and R_C/R_E relations. All the low-pressure relations in Table IX depend on the validity of the ideal cyclic process, and all imply that R_E in expt. 93 at 5.9 mm. is too low by 28%. The corrected R_E/R_O value from Table X is too low by only 22%.

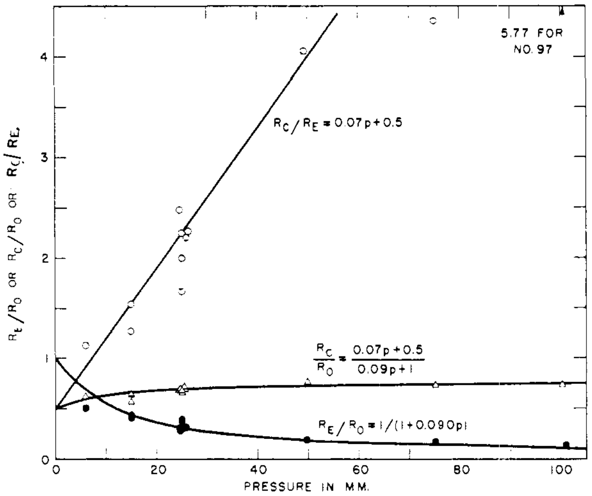


Fig. 17.—Relations among rates of cleavage, epoxidationsand total oxidations at low oxygen pressures in the oxidation of α-methylstyrene at 50°.

8.5. Composition of Polyperoxide.—The pyrolysis of α-methylstyrene polyperoxide (made at 1 atm. of oxygen) to acetophenone and formaldehyde, in yields up to 93% (section 8.3), and its reduction to α-methylstyrene glycol in 60% yield (section 7.8), establish its structure as substantially $(\text{-OOCH}_2C(CH_3)C_6H_5)_n\text{-}$ which theoretically contains 71.98% C, 6.71% H, 21.31% O. This section will consider end groups and then the structure of the polymer made at low oxygen pressures. These considerations support the conclusions of the previous section. The low pressure polymer consists mostly of $\text{-CH}_2C(C_6H_5)(CH_3)O\text{-}$ units, $\text{-CH}_2O\text{-}$ units, and α-methylstyrene peroxide units which have escaped depolymerization.

In expt. 127 (section 7.4 and Table VII), ABN decomposed at the rate of 0.000107 mole/l./hr.[9] Polyperoxide units were produced at the rate of 0.0589 mole/l./hr. and the total rate of reaction of monomer was 0.0982 mole/l./hr. The number-average molecular weight of the peroxide (fractions B and E) was 1680, and the molecules averaged $(C_9H_{10}O_2)_{11.2}$. Thus, 40 molecules of polyperoxide were produced per ABN decomposed. The molecular weight and end groups therefore depend on some chain transfer mechanism.

By the methods used with styrene,[4] the ratio of the rate constants for the chain transfer step which determines molecular weight and for the competing propagation reaction (3 or 4) for α-methylstyrene can be calculated. The ratio is not $1/\overline{DP}$, as with styrene, but $1/\overline{DP}$ times a correction for the rather prominent cleavage reaction, (rate of peroxide formation)/(total rate of reaction of methylstyrene). The ratios in two experiments[54] checked very well at 0.040. The near identity of this value with that found for styrene suggests that these two monomers may have the same chain transfer mechanism, even though an allylic hydrogen atom is available in only one of them. While the end groups in α-methylstyrene peroxide have not been determined satisfactorily, the data just above and in section 7.4 are at least consistent with reactions 41–43 proposed for styrene. For simplicity, the discussion will assume that α-methylstyrene oxidation chains made near 1 atm. of oxygen begin with HO_2-$CH_2C(CH_3)(C_6H_5)$- and $O{=}CHC(CH_3)(C_6H_5)$- groups and end with $-CH{=}C(CH_3)C_6H_5$ groups.

All the polyperoxides which were analyzed (except the methanol-soluble fraction E of expt. 127) contained between 71.2 and 73.0% C (Table VII), even though they were made under oxygen pressures ranging from 6 mm. to 745 mm. Nevertheless, these polymers differed in infrared absorption and in peroxide content. As the oxygen pressure during oxidation decreased, the general absorption at 8.50 to 10.50 μ increased; new bands appeared at 9.15 and 10.15 μ, probably due to ether links; the strong band of the polyperoxide at 9.7 μ became less intense, and absorption at 2.76 and 2.87 μ (due to hydroxyl) and at 5.78 μ (probably due to $C_6H_5C(CH_3)CHO$) increased. These changes were readily apparent at 150 mm. pressure, and pronounced at 50 mm., these pressures being considerably higher than with styrene. Peroxide determinations by the thiocresol method used for styrene (section 2.7) indicated that much of the oxygen was not present as peroxide. By this method, several α-methylstyrene peroxides made at 1 atm. of oxygen oxidized 80% of the theoretical thiocresol, based on their oxygen contents.[55] Peroxide no. 120, made at 15 mm. pressure, oxidized only 34% of the theoretical mercaptan. Here, only 40–45% of the oxygen seemed to be in peroxide links. Peroxide no. 93, made at 6 mm. pressure of oxygen, oxidized only 15–30% of the theoretical thiocresol.

The structures of these low pressure peroxides have not been determined but we can deduce their structures fairly well. If we neglect the end groups and consider the units which may be present in α-methylstyrene–oxygen polymer at low pressure, $-CH_2C(CH_3)(C_6H_5)O_n-$ or $-CH_2O_n-$, where n = 0, 1 or 2, we find that the simplest way to reduce the peroxide content of the polymer without changing the carbon content is to replace a $-CH_2C(CH_3)(C_6H_5)O_2-$ unit by one $-CH_2C(CH_3)(C_6H_5)O-$ unit and approximately one $-CH_2O-$ unit. This postulate is examined below and found to be adequate. While some of the other structures may be present, they cannot be present in large proportions and they do not contribute to the required carbon-peroxide relations.[56]

Table X shows the results of recalculating data for two experiments on the assumptions that the polymers contain only $-C_9H_{10}O_2-$, $-C_9H_{10}O-$, and $-CH_2O-$ units and that the weight fraction of peroxide is 1.25 times that found by titration. This approach ignores end groups in the polymer, but even the whole polymer is a small fraction of the total product. The proportions of the two types of ether units are then calculated from carbon analyses. Comparison of Tables VII and X shows that the best correction we can make for the structure of the copolymer requires little change in Table VII or previous discussion. The biggest change is in the calculated rate of oxygen consumption in the experiment with the least oxygen. In general, where the structure of the polymer deviates most from $(-C_9H_{10}O_2)_n$, the polymer is formed in only minor proportions. Both experiments in Table X show that 15–19% of the total expected formaldehyde is retained in the polymer. This result is in reasonable agreement with analyses for free formaldehyde, considering difficulties in collecting and analyzing this gas (section 4.5). Experiments 70–71 and 77–79, which cover the range 15–479 mm. of oxygen, yielded 73–77% as much free formaldehyde (as methone derivative) as acetophenone.

Table X indicates that for every molecule of epoxide formed by reaction 8, about 80% of the residual MO· units from reaction 9 decompose to acetophenone by reaction 9a (*i.e.*, (epoxide − $-C_9H_{10}O-$)/epoxide = 0.80) and that 50–60% of the residual MO· units also lost formaldehyde

TABLE X

RECALCULATION OF DATA IN TABLE VII

Expt.	93	120	
O_2 pressure, mm.	5.9	15.0	
Polymer, C, %	73.0	71.2	
Wt. % peroxide in polymer	28(±10)	42.5	
	Rates in mole/l./hr.		
$-C_9H_{10}O_2-$	0.0010	0.0022	Polymer
$-C_9H_{10}O-$	.0024	.0025	
Bound CH_2O	.0017	.0038	
Free CH_2O[a]	.0091	.0164	
$Ac-C_6H_5$	.0108	.0202	
Epoxide	.0096	.0131	
R_M (monomer)	.0238	.0380	Total rates of reaction
R_O (oxygen)	.0178	.0302	

[a] Calculated from the assumption that $Ac-C_6H_5$ = bound CH_2O + free CH_2O.

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(54) Two experiments carried out by the procedure used for styrene,[4] at oxygen pressures of 0.25 and 1.0 atm., gave the following rates in mole/l./hr.: peroxide, 0.018 and 0.067; oxidation, 0.065 and 0.117; mol. wts. by freezing point in benzene, 1040, 2170. In expt. 127, which lasted 24 instead of 7 hours, the average mol. wt. of the polyperoxide fractions was 1680, the ratio of rate constants, 0.054.

(55) From yields of acetophenone obtained from such peroxides on pyrolysis (Table VIII), about 93% of their oxygen may be in peroxide links.

(56) A small proportion of $-C_9H_{10}-$ units may be compensated by one $-CH_2O_2-$ or two $-CH_2O-$ units. Substitution of $-CH_2OC(CH_3)(C_6H_5)O-$ for $-C_9H_{10}O_2-$ groups would be a neat solution if there were a plausible mechanism for obtaining the polyacetal structure. Carbon-hydrogen ratios in $-C_9H_{10}O_2-$ units and in the $-C_9H_{10}O-$ plus $-CH_2O-$ combination are so similar that hydrogen analyses have not been useful.

by reaction 9b. While the above estimates are based on some assumptions, the direct formaldehyde analysis in expt. 79 at 15 mm. establishes that *at least* 33%, and probably nearer 60%, of the residual MO· units decomposed to formaldehyde as well as to acetophenone.[57]

8.6. Thermal Oxidation of α-Methylstyrene at 50°.—Figure 18 represents oxygen absorption as a function of time when 100 g. of α-methylstyrene, without added initiator, was shaken vigorously in a thermostat at 50°, with oxygen at a total pressure of 741 mm. The oxidation is clearly autocatalytic. The agreement of the experimental points with the curve calculated from equation 49 shows that both a thermal reaction and a peroxide formed on oxidation contribute to initiation, and that the over-all rate of oxidation is proportional to the square root of the total rate of initiation. For such an oxidation, the rate of oxygen absorption in moles/l. of solution/hr., was found to be

$$d[O_2 \text{ absorbed}]/dt = 1.8 \times 10^{-6} + 6.3 \times 10^{-4}(O_2 \text{ absorbed})^{1/2} \quad (48)$$

The integrated form is

$$[O_2 \text{ absorbed}] = 1.58 \times 10^{-4}t^2 + 1.35 \times 10^{-3}t \quad (49)$$

The autocatalysis is apparently not reproducible, but the form of equation 48 may be generally applicable. In expt. 94 (Table VII), the amount of oxidation at 8, 14.5 and 24 hours corresponded closely to equation 49 with 6×10^{-4} as the coefficient for t^2. Such variations suggest that the autocatalysis may be due to traces of metals, and possibly to small proportions of hydroperoxide in the oxidation products. Experiment 118 indicates that the spontaneous oxidation at 4 atm. of oxygen is much like that at 1 atm. of oxygen but irregularities in autocatalysis have thus far obscured the effect of oxygen pressure.

In none of these experiments is the rate of either thermal or autocatalytic initiation comparable to the rate of initiation by 0.01 *M* ABN. In Fig. 18, for example, the rate of oxygen absorption after 24 hours is 0.011 mole oxygen/l. of soln./hr., about one-tenth the rate of oxygen absorption in expts. 74 and 86 in Table VII. Therefore, the rate of initiation in the latter experiments is about a hundred times the rate of initiation at 24 hours in Fig. 18, and thermal initiation can be neglected when 0.01 *M* initiator is present. Experiment 81, described in section 7.3, shows that initiation by accumulated peroxide can be neglected when 0.01 *M* ABN is present; the rate decreased regularly with time over 24 hours.

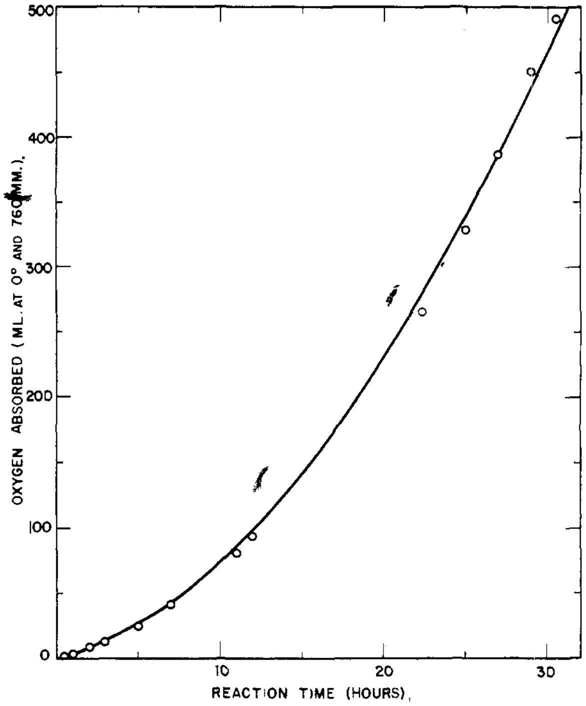
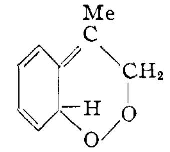


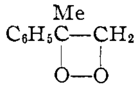
Fig. 18.—Thermal oxidation of 100 g. of α-methylstyrene (0.1135 l.) at 50°. The curve corresponds to equation 49.

Since the proportions of acetophenone and α-methylstyrene oxide in the final products of oxidation of expt. 94 are the same, within experimental error, as in experiments initiated by ABN, and since R_C/R_O at higher pressure is independent of added initiator (Fig. 15), the thermal oxidation differs only in the mode of initiation.

The recent paper by Hock and Siebert[46] will now be considered in the light of our results. Their autoxidation of 49 g. of α-methylstyrene for 120 hours at 45°, in the absence of added initiator, gave 10 g. of oxidation products consisting of 51% polyperoxide, 36% acetophenone, 6% epoxide, a trace of atrolactaldehyde, and 7% monomeric moloxide.[58] To the latter, they assigned the structure



Their compound melted at −5°, distilled at 70° at 0.05 mm., had the carbon content and molecular weight for this structure, decomposed readily into acetophenone and formaldehyde, did not react with iron pentacarbonyl, and decolorized permanganate in acetone. The last reaction is apparently the basis for excluding the structure



$$\begin{array}{cc} \overset{\text{Me}}{C_6H_5C} & \!\!\!-\!\!\!- CH_2 \\ | & | \\ O & \!\!\!-\!\!\!- O \end{array}$$

which nevertheless seems more probable than the non-aromatic structure of Hock and Siebert. No evidence of hydroperoxide or of moloxide (*cf.* section 7.4) was found in the present work, but infrared spectra of some fractions are consistent with the presence of some atrolactaldehyde. An analogous product, α-hydroxyacetophenone, has been found in the oxidation of styrene[4] and in the decomposition

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(57) The lower limit is calculated as follows. For each 285 molecules of epoxide formed, 361 molecules of acetophenone and at least 270 molecules of free formaldehyde were formed. The residue could contain no more than 91 molecules of bound $-CH_2O-$ units and no more than 149 $-C_9H_{10}O-$ units. Therefore, at least 136 terminal MO· radicals decomposed (285−149), leaving no more than 91 bound $-CH_2O-$ residues, and evolving at least 45 molecules of free CH_2O. The upper estimate is calculated as follows: There is not quite enough missing formaldehyde to permit residue 79 to contain the same proportion of formaldehyde as shown for residue 120 in Table VII. If all the missing formaldehyde, 91 molecules per 285 molecules epoxide, is in residue 79, then the carbon analysis shows that the remainder of the residue is 50 wt. % each $-C_9H_{10}O-$ and $-C_9H_{10}O_2-$, 74 units and 66 units, respectively. On this basis, only 74 out of a potential 285 MO− units were retained in the polymer. The 211 which decomposed gave 211 molecules of acetophenone and 120 molecules of free formaldehyde.

(58) Although the use of light to promote these oxidations is not mentioned in this paper, previous related work employed a mercury vapor or incandescent lamp.

TABLE XI

OXIDATION OF α-METHYLSTYRENE NEAR 170°

		Oxygen			Reaction		Average rates in mole/l./hr.			
Expt.	Initial C_9H_{10}, g.	Pressure, mm.	Input, ml./min.	Exhaust, ml./min.	Time, hr.	Temp., °C.	$(C_9H_{10}O)_n$	AcC_6H_5	$C_9H_{10}O$	Total C_9H_{10}
8T	179	Very low	33.5 air	...	4.0	169–170	0.0376[b]	0.0466	0.0485	0.1610
95	90.4[a]	1–8	50 O_2	10–14	1.18	170–176	0.417[c]	0.524	0.563	1.504
98	90.4[a]	25–68	90–97 O_2	3–8	0.50	167–168	1.02	1.13	1.33	3.48

[a] 1.0 g. of magnesium oxide also present. [b] This residue also contained 0.72 C_9H_{10} unit per $C_9H_{10}O$ unit. Experiment by Mr. A. T. Tweedie. [c] 80.6% C.

of styrene peroxide.[5] An unidentified compound, $C_9H_{12}O_2$, was obtained in minute yield from the ABN-initiated expt. 127 (section 7.4). Experiment 94, without added initiator, corresponds better to the experiment of Hock and Siebert, but gave no indication of their "moloxide."[59]

Hoffman[60] reported a small yield of hydroperoxide, apparently 2-phenylallyl hydroperoxide, and also acetophenone and epoxide, by the uncatalyzed oxidation of styrene at 90°. It is, however, difficult to distinguish between primary and secondary products from his report.

8.7. Thermal Oxidations Near 170°.—Three oxidations were carried out with refluxing α-methylstyrene, without added initiator, to see how this high-temperature oxidation might be affected by oxygen pressure. The procedure was described in section 7.9. Of particular interest are the high rate of oxidation observed (3.5 moles of α-methylstyrene/l. of monomer/hr., apparently limited by the oxygen supply) and the high proportion of monomer converted to epoxide (38%).

Table XI shows that the over-all rate of reaction of α-methylstyrene is nearly proportional to the oxygen supply and that nearly equal proportions of α-methylstyrene are converted to each of the three major products, low polymer, epoxide and acetophenone (and formaldehyde), over the whole range of pressures tested. Possibly dissolved oxygen reacts so rapidly that its effective concentration in solution is very low in all experiments, and is limited by the rate of solution.

The non-volatile materials in these experiments differ from those obtained at 50°. No peroxide survived the 170° reaction temperature. The following data show that when sufficient oxygen was available, the major high-boiling product had the carbon analysis of a polyether $(-CH_2C(CH_3)(C_6H_5)O-)_n$, and that when the reaction mixture was really starved for oxygen, 1.7 α-methylstyrene units were incorporated in the polymer per ether link. In expt. 95 at 170°, the reaction mixture was distilled up to a liquid temperature of 160° at 0.5 mm. pressure. This residue contained 80.6% carbon, corresponding closely to the polyether, although it contained hydroxyl and carbonyl groups. It did not have the strong general absorption at 8.5–10.50 μ characteristic of polymer made at 50° and low oxygen pressures. A similar residue from expt. 8T contained 85% C and had an average molecular weight in benzene of 360. The latter data correspond to $(C_9H_{10}O_{0.58})_{1.85}$; 72% of this residue could be distilled at 80–250° at 0.7 mm. pressure, and the distillate had the same carbon content as the starting material.

Polyether may be formed by modifying the cyclic process in section 8.4 into a new cycle, reactions 10, 3, 4 and 50

$$R''OMO_2M\cdot \longrightarrow R''OMO\cdot + \text{epoxide} \qquad (50)$$

This proposal implies that the decomposition of ROMO· radicals requires appreciable time, and that at high temperatures this decomposition is partially prevented by addition of monomer, reaction 10. The importance at high temperatures of cleavage by reactions 11 or 12, accompanying propagation, is unknown.

9. Summary and Conclusions

This section will summarize the most important novel features of the oxidation of α-methylstyrene, in comparison with the oxidation of styrene (paper V). The first feature is the depolymerization of polymeric radicals ending in an alkoxy group, $MO(OMO)_n\cdot$. These are produced in the thermal or photodecomposition of α-methylstyrenepolyperoxide and also by reaction 8, loss of epoxide from a polyperoxide radical ending in a monomer unit. Depolymerization of these radicals to MO· and cleavage products proceeds rapidly to completion at 50°, even in excess α-methylstyrene, a good radical scavenger, as solvent (sections 8.3–8.5). Little or no activation energy is required. These studies have avoided complications due to polymerization of styrene (sections 4.4–4.6).

The next point is concerned with the fate of the terminal MO· radical and its repeated use as a site for oxidation of α-methylstyrene. At oxygen pressures of a few millimeters, this MO· residue is decomposed to some nearly constant fragment. Here, many molecules of α-methylstyrene and oxygen are converted to acetophenone, formaldehyde and α-methylstyrene oxide in a reaction which approaches (46) as a limit. The sequence of reactions in section 8.4 makes this limit plausible. The end group, R″–, in this sequence is not known, but $HO_2CH_2C(CH_3)(C_6H_5)-$, $O{=}CHC(CH_3)(C_6H_5)-$ (section 8.5), and H–[61] are good possibilities. This end group, R″–, apparently accumulates a few $-OCH_2-$, $-OCH_2C(CH_3)(C_6H_5)-$ and $-O_2CH_2C(CH_3)(C_6H_5)-$ units during an oxidation at low pressure, but the reaction is surprisingly clean. Experiment 120 in Table X illustrates this point. The initiator, ABN, decomposed at the rate of 0.000107 mole/l./hr.[9] and produced free radicals at less than twice this rate. For each initiating radical produced, at least 94 molecules of α-methylstyrene were converted to acetophenone and at least 61 to α-methylstyrene oxide, but the radical residues on which this conversion took place eventually bound only 12% of the monomer reacted, plus methylene fragments of about 10% more of the monomer. The oxidation of styrene is less clean-cut because the R″OMO· radicals decompose less easily and because of polymerization (section 4.5).

At higher pressures, the principal product of oxidation of α-methylstyrene is the polyperoxide, as with styrene. However, at 4 atm. of oxygen,

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[59] As prepared by procedure B, this fraction originally weighed 11.23 g. and consisted of 53% non-volatile peroxide, 9% acetophenone, 36% α-methylstyrene and 2% oxide and material not accounted for; 8.61 g. was extracted with petroleum ether, but only 0.02 g. of soluble material was not volatile at 50° and 0.5 mm. pressure. Only 0.28 g. more was soluble in methanol and not volatile under the same conditions. Of this 0.28 g., 33% was acetophenone and the remainder had essentially the infrared absorption of other methanol-soluble peroxides. The insoluble material had a molecular weight of 1320, by freezing point in benzene. The original material was stored at 7° for 6 weeks before the solvent extractions.

[60] J. Hoffman, Abstracts of Atlantic City Meeting of American Chemical Society, Sept. 1956, p. 16-O.

[61] If $R''\cdot = H\cdot$, no H atoms would be formed, but $HO\cdot$, $HO_2\cdot$ and $HOCH_2\cdot$ might replace $R''O\cdot$, $R''O_2\cdot$ and $R''\cdot$ in the sequence.

about 15% of the monomer is converted directly to cleavage products as compared with only 3% for styrene. These cleavages are independent of oxygen pressure, and while they are represented by reactions 11 or 12, their mechanisms are unknown. Comparison of Figs. 1 and 9 shows that, as the oxygen pressure is reduced, epoxide formation and cleavage become important and reach maxima at higher pressures with α-methylstyrene than with styrene. This difference will be discussed in section 17.3. The effective value of the ratio, k_e/k_{po} increases with oxygen pressure in the oxidation of α-methylstyrene (Table IX), as also found in the oxidation of styrene (equation 32 and Fig. 5). At 50°, these ratios are 9–14 times larger for α-methylstyrene than for styrene. Thus, in the latter oxidation, monomer radicals are not only more prevalent (at the same pressure) than in styrene, but they also rearrange relatively faster.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY AND STANFORD RESEARCH INSTITUTE]

The Oxidation of Unsaturated Compounds. VII. The Oxidation of Methacrylic Esters[1,*]

BY FRANK R. MAYO[3] AND A. A. MILLER

RECEIVED SEPTEMBER 5, 1957

The reaction of methyl methacrylate with oxygen has been studied at 50° in the presence of 0.01 M ABN at oxygen pressures from 0–3100 mm. Above about 500 mm. of oxygen, the rate of reaction of monomer (0.006 mole/l./hr.) and the products of oxidation (80% polyperoxide, $(C_5H_8O_4)_n$, and 20% methyl pyruvate and formaldehyde) are nearly independent of oxygen pressure. As the oxygen pressure approaches zero, the rate of reaction of oxygen decreases, and the rate of reaction of monomer approaches 0.40 mole/l./hr. Thus oxygen strongly retards polymerization of methyl methacrylate. The relative reactivity of monomer and oxygen toward monomer radicals, and the tendency toward crossed termination, are nearly independent of the composition of monomer radicals. Butyl methacrylate is about as reactive as the methyl ester. The over-all activation energy for its oxidation is 26.5 kcal./mole.

10. Introduction

Barnes, Elofson and Jones[62] found that methyl methacrylate absorbed oxygen at 40° to give a polymeric peroxide analyzing for $[(C_5H_8O_2)_{1.18}O_2]_n$. Further study of the oxidation of this monomer was undertaken to provide standards for study of its co-oxidation with styrene or α-methylstyrene (paper IX). When a substantial proportion of a cleavage product, methyl pyruvate, was found, the effect of pressure on this cleavage reaction was investigated.

11. Experimental

11.1. **Materials.**—Methacrylic esters were obtained from various commercial sources. They were washed free from inhibitor with aqueous sodium hydroxide, then washed with water, dried and distilled at reduced pressure. They were stored at about 7° and redistilled before each group of experiments. Beginning with experiment Q in Table XII, the monomer was dried with calcium hydride. No improvement in reproducibility was noted.

11.2. **Procedures.**—Experiments 1, A-1 and 8 were carried out with 200, 150 or 100 ml. of methyl methacrylate, respectively. In expt. 1, samples containing 0.1–0.2 g. of polyperoxide were withdrawn at intervals and analyzed according to procedure C (section 2.2). In expt. 8, the oxidation was carried out according to procedure A, and 20 g. of product was then analyzed by procedure C. In this experiment, oxygen was admitted at the rate of 0.006 mole/hr., and consumed at about one-tenth of this rate. Experiment A-1 was carried out similarly, with duplicate analyses for pyruvate (±2%) and polymer (±0.7%). In A-1, oxygen was admitted at the rate of 0.0025 mole/hr. and consumed at one-fourth to one-fifth of this rate. All high pressure experiments were carried out in a closed system by procedure C, starting with 10 or 20 ml. of monomer or solution.

In procedure C, with methyl methacrylate, the reaction mixture was distilled at 0.5 mm. pressure, with final warming of the residue to 50°. This distillate was then concentrated to 1–2 ml. at a pressure of 150 mm. in a short jacketed distilling column with a nichrome spiral for packing. The ester distilled at about 53°. The concentrate apparently contained a trace of volatile peroxide or of ABN, for the residue polymerized partially during concentration. For example, 8 g. of distillate from expt. 1 gave 0.77 g. of dry polymer in a 1-hour concentration, while similar concentration of fresh monomer gave only 0.05 g. of polymer. In the example cited and in other cases when the concentrate became viscous, the liquid was distilled from the polymer at 50–70° and 0.5 mm. pressure, and concentration was continued with the distillate. The polymer thus obtained was discarded. It was dry, brittle, and in a porous or expanded state so that it should have contained little volatile material. The concentrate, mostly methyl methacrylate, was examined for its infrared absorption. Methyl pyruvate was determined by the absorption of its band at 13.9 μ, with the use of a series of standard solutions. The ability of the fractionating column to separate pyruvate from methacrylate was tested by reconcentrating a distillate from a concentration. The second concentrate was free from pyruvate.

The epoxide of methyl methacrylate, methyl 2-methyl-2,3-epoxypropionate, was prepared by Dr. J. R. Ladd. A 5% solution of this epoxide in methyl methacrylate exhibited strong and sharp absorption bands at 11.5 and 13.2 μ. If the rate of epoxide formation had approached 5% of the rate of pyruvate formation, epoxide would have been detected easily. However, there was no significant spectroscopic evidence of any oxidation product other than pyruvate in the concentrates of the volatile materials from the oxidations.

In experiments with 0.04 M ABN, removal of initiator by volatilization at 50° and 0.5 mm. pressure was tedious. The difficulty was partially overcome by extracting the peroxide–initiator mixture with cold carbon tetrachloride. A large fraction of the initiator and a small fraction of the polymer did not dissolve. Most of the ABN was sublimed out of the insoluble fraction and then the two fractions were combined and heated to constant rate of weight loss. An extreme example is Z, with 20 ml. of solution, and 0.135 g. of ABN initially. After heating the whole product for 135 min. and the ABN-rich residue for 165 min. additional, the final weight of peroxide was 0.1425 g. and the final rate of weight loss was 0.6 mg. per 30-minute heating. The extrapolated initial weight was taken as 0.1461 g.

11.3. **Calculations.**—Calculations of rates followed the procedures used with styrene. At 50°, the density[63] of

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[*] For numbering of footnotes, equations, etc., *cf.* note 2 of paper V.

(62) C. E. Barnes, R. M. Elofson and G. D. Jones, THIS JOURNAL, **72**, 210 (1950).

(63) E. H. Riddle, "Monomeric Acrylic Esters," Reinhold Publishing Corp., New York, N. Y., 1954, pp. 8–9.