Anal. Calcd. for $C_{11}H_9NO_3$: C, 65.0; H, 4.46; N, 6.9. Found: C, 65.1; H, 4.46; N, 6.7.

4-Methoxy-2-naphthylamine.—A suspension of 1-methoxy-3-nitronaphthalene (5 g.) in methanol (150 ml.) was hydrogenated over 10% palladium-on-charcoal (0.1 g.) at an initial hydrogen pressure of 2 atm. After filtration of the solution from catalyst, the methanol was distilled and the residue extracted with ligroin or petroleum ether (the latter giving a purer product) to give long large colorless prisms, m.p. 57.5–58.5°, which showed a strong blue fluorescence in methanol solution.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.3; H, 6.40; N, 8.1. Found: C, 76.2; H, 6.28; N, 8.0.

N-4-Methoxy-2-naphthylchloroacetamide.—To a solution of 0.36 g. of 4-methoxy-2-naphthylamine in 10 ml. of acetone there was added 0.4 ml. of chloroacetyl chloride. A precipitate formed immediately, with evolution of heat. After the initial reaction had subsided, 40 ml. of 2.5% aqueous sodium bicarbonate was added gradually, with swirling, whereby the initial precipitate dissolved and a new solid precipitate fell out. This crude product was isolated and recrystallized from aqueous ethanol, giving fine colorless needles, m.p. 153–154°.

Anal. Calcd. for $C_{13}H_{12}O_2NCl$: C, 62.5; H, 4.85; N, 5.6. Found: C, 62.5; H, 4.81; N, 5.6.

N-4-Methoxy-2-naphthyltrifluoroacetamide.—To a solution of 0.36 g. of 4-methoxy-2-naphthylamine in 10 ml. of acetone there was added 1.0 ml. of trifluoroacetic anhydride, with evolution of some heat. After 5 min., 40 ml. of 2.5% aqueous sodium bicarbonate was added gradually, with swirling, to precipitate an oil. The oily layer was taken up in ether, washed with water and evaporated to a viscous residue. Recrystallization from ligroin gave a solid precipitate (m.p. 131–134.5°), which was recrystallized from aqueous ethanol (charcoal) to give colorless microscopic needles, m.p. 133.5–135°.

Anal. Calcd. for $C_{13}H_{10}O_2NF_3$: C, 58.0; H, 3.74; N, 5.2. Found: C, 58.0; H, 4.03; N, 5.3.

Carbobenzoxy-L-leucyl-4-methoxy-2-naphthylamide.—The synthesis was carried out with equimolar quantities of reagents according to the method of Sheehan, Goodman and Hess.[22] A solution of 2.51 g. of N,N'-dicyclohexylcarbodiimide in 15 ml. of dichloromethane was added to 3.22 g. of carbobenzoxy-L-leucine and 2.10 g. of 4-methoxy-2-naphthylamine dissolved in 10 ml. of the same solvent. Reaction was immediate and rapid. After one hour, the mixture was filtered and the precipitate of dicyclohexylurea was washed with ether. The combined filtrate and washings were boiled down to give a pinkish solid residue. Trituration of the product with ether removed most of the unreacted starting materials without dissolving much of the desired product. The latter was taken up in ethyl acetate (35 ml.), washed with 1 *N* hydrochloric acid, 1 *N* potassium bicarbonate and water, filtered and evaporated nearly to dryness. Addition of petroleum ether gave a white precipitate of carbobenzoxy-L-leucyl-4-methoxy-2-naphthylamide. This substance began to shrink at 169° and melted at 171–171.6°.

Anal. Calcd. for $C_{25}H_{28}N_2O_4$: C, 71.4; H, 6.71; N, 6.7. Found: C, 71.5; H, 6.66; N, 6.9.

L-Leucyl-4-methoxy-2-naphthylamide.—The carbobenzoxy group was removed[23] from the preceding compound (1.52 g.) by hydrogenolysis for 3 hours in methanol solution (150 ml.) at 2 atm. pressure of hydrogen with a catalyst of 10% palladium-on-charcoal (0.1 g.). The mixture was filtered from catalyst and boiled down to a mobile oily residue. Extraction of this oil with boiling petroleum ether gave, on chilling, an oily precipitate which soon changed to a highly crystalline solid, m.p. 96.5–97.5°, $[\alpha]^{28}D$ +15.1° (*c* 2.02, methanol).

Anal. Calcd. for $C_{17}H_{22}N_2O_2$: C, 71.3; H, 7.75; N, 9.8. Found: C, 71.3; H, 7.62; N, 9.9.

3-Methoxy-1-nitronaphthalene.—Methylation of 4-nitro-2-naphthol[12] by the method used for preparing 1-methoxy-3-nitronaphthalene gave small yellow plates, m.p. 101–102° (literature[12] m.p. 100–103°).

3-Methoxy-1-naphthylamine.—The method used above for hydrogenating 1-methoxy-3-nitronaphthalene was applied to 3-methoxy-1-nitronaphthalene. The compound, after crystallization from ligroin, was purified for analysis by recrystallization (charcoal) from petroleum ether. The needle-like prisms begin to sinter at 78° and melt at 79–79.5°. The compound shows a strong blue fluorescence in methanol.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.3; H, 6.40; N, 8.1. Found: C, 76.0; H, 6.36; N, 7.9.

N-3-Methoxy-1-naphthylchloroacetamide.—Prepared analogously to the isomeric derivative above, this compound occurred as very small needles melting at 144–145°.

Anal. Calcd. for $C_{13}H_{12}O_2NCl$: C, 62.5; H, 4.85; N, 5.6. Found: C, 62.2; H, 4.75; N, 5.7.

N-3-Methoxy-1-naphthyltrifluoroacetamide.—Prepared similarly to the isomeric derivative above, this compound was isolated as fine needles melting at 119–120°.

Anal. Calcd. for $C_{13}H_{10}O_2NF_3$: C, 58.0; H, 3.74; N, 5.2. Found: C, 57.8; H, 3.84; N, 5.3.

Acknowledgment.—The authors wish to acknowledge the assistance rendered by Mr. Joseph Walter, who performed the analyses.

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[22] J. C. Sheehan, M. Goodman and G. P. Hess, THIS JOURNAL, **78**, 1367 (1956).

[23] M. Bergmann and L. Zervas, *Ber.*, **65**, 1192 (1932).

BALTIMORE, MARYLAND

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

The Oxidation of Unsaturated Compounds. V. The Effect of Oxygen Pressure on the Oxidation of Styrene[1,2]

BY FRANK R. MAYO[3]

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The reaction of styrene at 50° in the presence of 0.01 *M* 2,2'-azobis-(2-methylpropionitrile) (ABN) has been studied at oxygen pressures ranging from 0–3200 mm. In the absence of oxygen, styrene is converted to polystyrene at the rate of 0.095 mole/l./hr. Above about 10 mm. pressure, styrene reacts at a nearly constant rate of 0.06 mole/l./hr., and the product is mostly styrene polyperoxide, $(C_8H_8O_2)_n$. The rate of reaction of styrene passes through a minimum of 0.03 mole/l./hr. at about 0.5 mm. pressure of oxygen. The O_2:C_8H_8 ratio in the polymer increases from zero to nearly unity as the oxygen pressure increases from 0–100 mm. Other products of oxidation also depend on pressure. A maximum of about 27% of the reacting styrene is converted to styrene oxide at 1 mm. pressure, and up to 46% to benzaldehyde and formaldehyde at 12 mm. pressure. Mechanisms for these reactions are discussed. The rate of reaction with oxygen or a peroxide radical of a radical ending in a styrene unit depends on the penultimate unit. The decomposition of styrene polyperoxide and the oxygen inhibition of bulk and emulsion polymerization are also discussed.

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[1] Portions of these papers were presented at Meetings of the American Chemical Society at Minneapolis on September 13, 1955, at Atlantic City on September 18 and 20, 1956, and at New York on September 9 and 11, 1957.

[2] Because of repeated cross references in this and the four succeeding papers, sections, tables, figures, equations and footnotes are each numbered serially throughout papers V to IX.

[3] Stanford Research Institute, Menlo Park, California.

1. Introduction

Previous papers in this series have considered the rate and products of oxidation of styrene above 25 mm. pressure of oxygen,[4] the reactions of the polymeric peroxide formed,[5] and the oxidation of indene.[6] These papers established that the oxidation of styrene involves two primary reactions, formation of polymeric peroxide and cleavage to benzaldehyde and formaldehyde, that the competition between these two reactions depends on the oxygen pressure, that the oxidation of indene at one atmosphere of oxygen yields polyperoxide as the only polymer, and that polyindene cannot be formed concurrently by a free radical mechanism.

The objects of the present paper were to extend our previous studies down to zero oxygen pressure and to determine the mechanism of the cleavage reaction. In the course of this work, it was found that about 27% of the reacting styrene was converted directly to styrene oxide at about 1 mm. pressure of oxygen. The rates and products of reaction have been satisfactorily accounted for in terms of a rather simple mechanism. Since the quantitative treatment of the data is lengthy and involved (section 4), the essential conclusions are summarized in section 5.

2. Experimental

2.1. **Materials.**—Styrene from Koppers or from Matheson, Coleman and Bell was purified and stored as described previously.[4] When it showed any cloudiness on mixing with methanol, the styrene was redistilled. 2,2'-Azobis-(2-methylpropionitrile) (hereafter called ABN) was recrystallized from acetone or methanol. Reagent grade benzene and methanol were used without purification.

2.2. **Procedures.**—Three general procedures, to be designated A, B and C, were employed in the oxidation of styrene and of some other monomers:

Procedures A and B.—Styrene, 150 or 200 ml. weighed to 0.1 g., and ABN, weighed to 0.2 mg. to make a 0.0100 *M* solution at 50°, were stirred for 6–7 hours at 50.0° in a 1-l., 3-necked, creased flask with ground glass joints. The mixture was stirred at 1500 r.p.m. by a glass or Teflon paddle, using a magnetic drive which eliminated packing and leakage. In expt. 127 and subsequent experiments, a Vibro-Mixer with a 45 mm. vibrating plate provided the agitation. Oxygen or air was admitted through a capillary. Gases were exhausted through an ice-filled trap which served as reflux condenser and through a trap at −78° to collect styrene carried past the ice trap. Sometimes a third trap was employed to absorb formaldehyde, containing water in runs at atmospheric pressure, or cooled by liquid nitrogen in experiments where the pressure was low enough so that no oxygen would condense. The temperature of the reaction mixture was maintained at 50.0°, and the temperature of the thermostat in which the flask was partially immersed would be between 49.8 and 50.2°, depending upon immersion, air temperature, agitation and gas flow.

At the end of the oxidation, the reaction flask was cooled to 20–25° and the weight change was determined. After correction for the weight of the styrene and formaldehyde collected, the weight of oxygen absorbed was usually found to check the value calculated from analyses of products. Sometimes formaldehyde polymerized in the first two traps at 0 and −78°. In such cases, styrene could be separated by rinsing with benzene, and the dry paraformaldehyde could be weighed separately. The weight of styrene found in the trap at −78° ranged up to about 5 g., being highest at low pressures and high rates of gas flow.

For analysis, substantially all the reaction mixture was decanted into a 300-ml. round-bottom long-necked flask. This flask was fitted with a thermometer reaching to the bottom of the flask and with a still-head and connection of 20 mm. glass tubing leading to a receiver cooled to −78°. At about 0.3 mm. pressure, most of the reaction mixture would distil below room temperature in 10–20 min. The concentration was completed by warming the residue to 50°, gently with a free flame if there was enough residue so that the thermometer reading measured the temperature of the concentrate, otherwise for 5 min. with a water-bath. Rapid distillation below room temperature was desirable to reduce polymerization of styrene during concentration. The portion taken for concentration, the distillate, and the residue were all weighed to 0.01 g. as a check on procedure and other weights. Losses during the operation were of the order of 0.1 g.

Benzaldehyde and styrene oxide in the distillate were determined by infrared absorption, using a model 21 Perkin-Elmer recording spectrograph and 0.1-mm. absorption cells. When the conversion to these products was low, 50.0 g. of distillate was concentrated to 5–15 ml. in a spinning band column at 10–20 mm. pressure, to remove the bulk of the lower-boiling styrene. Either the original solutions or concentrates were then examined by infrared. Analyses were based on reference samples containing 1–10% by weight benzaldehyde or styrene oxide in styrene, using the band at 12.08 μ for benzaldehyde and at 11.40 μ for the epoxide. Determinations of benzaldehyde are considered reliable to about 10% of the recorded rates near 0.001 mole/l./hr., to about 3% at rates above 0.005 mole/l./hr. Epoxide determinations are considered reliable within ±30% of the recorded rates near 0.001 mole/l./hr., within 10% above 0.005 mole/l./hr. Determinations of benzaldehyde and epoxide were sometimes made on both the whole distillate and the concentrate, and benzaldehyde was sometimes determined gravimetrically with 2,4-dinitrophenylhydrazine,[4] with agreement within the indicated limits. Distillates from the concentrations were examined for benzaldehyde, using the strong band at 5.85 μ, and the aldehyde concentration was found to be negligible when an adequate reflux ratio was employed. Since the epoxide boils above the aldehyde, loss of oxide is assumed to be negligible.

Procedures A and B differ in the analysis of the residue from the first low temperature distillation. This residue contains all the styrene peroxide, part of the benzaldehyde and styrene oxide, and some unchanged styrene. In procedure A, this residue was resolved, by three precipitations with methanol and appropriate distillations, into methanol-insoluble polyperoxide, methanol-soluble material not volatile at 50° and 0.5 mm. pressure (containing low molecular weight peroxide, styrene, benzaldehyde and epoxide), and concentrates of distillates which contained aldehyde, epoxide and styrene. The details of this procedure have been presented previously.[4] The methanol-insoluble peroxide was obtained as a 60–80% solution in benzene which was assayed as indicated for procedure B.

Benzaldehyde and epoxide in the volatile concentrates were determined by infrared without use of a solvent. The methanol-soluble peroxide was made up into a 10% by weight solution in chloroform, and the benzaldehyde and styrene oxide in this fraction were determined by infrared absorption and comparison with known standards. U. S. P. chloroform containing 0.5–1.0% ethanol was employed. The solvent was a poor choice because the absorption at 11.40 μ by ethanol partly masked the epoxide band. Although corrections were introduced, it was not possible to determine with any accuracy less than 0.5% epoxide in the chloroform solution, *i.e.*, less than 5% epoxide in the methanol-soluble polymer. Since about 90% of the epoxide was in the initial distillate, this error was not important.

Procedure B followed A up to the analysis of the residue of the low-temperature concentration. About 0.2 g. of this residue was analyzed as a 10% solution in chloroform for benzaldehyde and styrene oxide. Enough of the residue (or of benzene solution in procedure A) to give about 0.2 g. of non-volatile matter was then weighed out in a 125-ml. glass-stoppered conical flask and assayed as follows: The weighed solution was diluted with about 2 ml. of carbon disulfide which was then removed at reduced pressure, finally heating in a 50° bath for 1 min. at 0.5 mm. pressure. The remaining film was redissolved in carbon disulfide, which was removed as above. The resulting film was retreated with carbon disulfide which was then removed for 10 min. at 50° and 0.5 mm. The cooled flask was weighed, then heated for two to four additional 10- or 15-minute intervals

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[4] A. A. Miller and F. R. Mayo, THIS JOURNAL, **78**, 1017 (1956).

[5] F. R. Mayo and A. A. Miller, *ibid.*, **78**, 1023 (1956).

[6] G. A. Russell, *ibid.*, **78**, 1035, 1041 (1956).

at 50° and 0.5 mm., followed by weighings, until the residue attained constant rate of weight loss, presumably corresponding to thermal decomposition of the peroxide.[5] The ABN was also volatilized during the early stages of heating, and a sublimate of high purity collected on the connections. For 0.25 g. of final dry film, the weight losses averaged 10 mg. per 10 min. heating period, and so the extrapolated initial weight, used for calculations, was 30–50 mg. (1–2%) greater than the final weight. Considering the small range in the nearly constant rates of weight loss *after* the first 10-minute heating period (0.0007–0.0016 g. per 10-min. period), further heatings are probably unnecessary. The final films were used for infrared absorption spectra (10% solutions in chloroform) and for carbon and hydrogen determinations. The films were essentially free from benzaldehyde, epoxide, benzene, carbon disulfide and ABN.

Procedure B does not distinguish between methanol-soluble and methanol-insoluble products, but it is much less laborious and probably more accurate. It may result in loss of traces of volatile unidentified oxidation products. The carbon disulfide serves to expose fresh surface and sweep out volatile material. In spite of its very strong absorption band at 6.58 μ, carbon disulfide was seldom found in the final product.

Procedure C was used for reactions carried out above atmospheric pressure. These experiments were performed in a heavy glass flask with a volume of 50 ml. in the bulb, 25 ml. in the long neck. A side arm connected the flask to vacuum and oxygen supply. The flask was closed with a Neoprene disk, held by a metal washer and a screw clamp, and sealed with Apiezon grease. In most methacrylate experiments, the disk was covered with aluminum foil. ABN was either weighed directly to 0.1 mg. or added as a standard solution in benzene. This solvent was then evaporated at or below room temperature by an air stream and low vacuum. Ten ml. of styrene (or α-methylstyrene), measured at 25° (or 10 ml. of methyl methacrylate, measured at 30°, or an equal volume of benzene, measured at 27°) was then added by pipet. These volumes became 10.27 ml. at 50°. For slow reactions, quantities were sometimes doubled. The flask was then closed and its contents were cooled to −78°. The air was removed (three evacuations to 50 mm.) and replaced by oxygen. The flask was then shaken in a bath at 50° for a period sufficient to give about 0.2 g. of peroxide. The pressure was usually maintained with oxygen to within about 2 p.s.i. of an average pressure of 46.6 p.s.i. gauge, or a total pressure of about 3160 mm. The reaction mixture was chilled before the pressure was released. The oxidized styrene was then decanted into a tared 125-ml. conical flask, and weighed. More than 99% of the volatile material was removed by distillation at 0.5 mm., with shaking to avoid bumping, and with a final warming to 50° for 5 minutes. The same type of still-head and receiver was used as was described for procedure A. The residue was then put through the carbon disulfide and evaporation treatments described for the assay in procedure B. The distillate was decanted into a 20-ml. flask and fractionally distilled through a 20-cm. column with a platinum or Nichrome spiral for packing. The distillation temperature was 50–55° at about 30 mm. pressure. Ten ml. of distillate was thus concentrated to 1–3 ml. and analyzed for benzaldehyde and styrene oxide by infrared absorption, as in procedure A.

Procedure C was the fastest of the three procedures because it employed the smallest quantities of material and required the least basic information: an infrared absorption on the concentrate and the weight of the non-volatile material after the assay. The method was not used at less than about 3000 mm. pressure of oxygen because it did not permit circulation of oxygen or removal of formaldehyde gas, which might have attained a significant partial pressure in reactions at low total pressure.

The monomer–oxygen ratios in the polymer were determined from carbon analyses. Since polystyrene and 1:1 peroxide differ by only 21.7% in carbon content, the styrene–oxygen ratio is known only to about 2%.

2.3. Oxygen Pressures.—With procedures A and B, total pressures below atmospheric were usually maintained constant within 1 mm. below 25 mm., within 5% at 25–500 mm., by means of a Cartesian manostat. Pressures were read to 0.1 mm. by a Zimmerli gage connected directly to the reaction flask. The average pressure was determined graphically and the effects of small variations in pressure are assumed to be negligible. The system was always found to be free from leaks before the reagents were added. The rate of gas flow was estimated within 20% by one or two of three methods. (1) Calibrated capillaries, dipping below the surface of the liquid, were used to introduce air or oxygen in reactions below atmospheric pressure. They were calibrated by measuring the volume of air, at room temperature and pressure, which could be exhausted through the capillaries into a vessel evacuated to 20–50 mm. pressure. The air flows thus measured corresponded to 0.011 to 0.12 mole/hr. (2) Another method was based on the amount of styrene carried past the 0° trap. The partial pressure of styrene passing this trap is taken as 1.13 mm.[7] and all of this is assumed to condense in the −78° trap. The ratio of the partial pressure of the other gases to the 1.13 mm. pressure of the styrene is the same as the ratio of the moles of other gases passed through the traps to the moles of styrene collected in the cold trap. Comparisons between the two methods indicated that they agreed well if ±0.1 g. error was allowed for the styrene found in the trap. The second method was most useful at low pressures or high flow rates where a few grams of styrene was collected. (3) Gas was led to the capillary through a flowmeter, calibrated for both air and oxygen.

The partial pressure of air or oxygen above and in the reaction mixture is taken as the measured average total pressure, less 24.3 mm., the vapor pressure of styrene at 50°.[7] Experiments 57 and 58 in Table IV were stirred at 1000 and 1500 r.p.m., respectively. Since they agree within experimental error, stirring was assumed to be adequate. Experiments with α-methylstyrene (paper VI) at 25 mm. pressure of oxygen also showed no significant effect of rate of stirring over the range 750–1800 r.p.m. Pure oxygen was supplied in experiments with more than 4 mm. oxygen pressure. Below this limit, an uncertainty of a few tenths millimeter in 25–30 mm. total pressure results in too large an uncertainty in the partial pressure of oxygen. This difficulty was met by introducing air or an air–nitrogen mixture into the reaction vessel and determining (with a mass spectrograph) the fraction of oxygen in the exhaust gas, after it had passed through a liquid nitrogen trap. The fraction of oxygen in this exhaust gas is taken to be the fraction of oxygen in the gas over the reaction mixture.

2.4. Polymer Fractions Obtained by Procedure A.—Procedure A separated the polyperoxide into methanol-soluble and methanol-insoluble fractions which were analyzed separately for carbon. Table I shows how the total weight of polymer and the proportion of higher molecular weight product decrease with the pressure of oxygen used. Table I also summarizes the weights and carbon contents of the pairs of polymer fractions obtained by procedure A. The data for the soluble polymer have been corrected for the benzaldehyde, oxide and ABN found by infrared analysis. The $C_8H_8O_2$ ratios for the total polymers in Table V come from the weighted average carbon analyses in Table I. The methanol-soluble fractions have molecular weights of 200–400. The methanol-insoluble fractions have molecular weights ranging up to 2000. Polymers made at 0.5 to 5 mm. pressure exhibited a strong absorption band at 9.1 μ which was not present either in polystyrene or styrene polyperoxide. This band may be due to ether links between styrene units.

2.5. Calculations of Reaction Rates.—Volumes were calculated using 0.878 g./ml. for the density[8] of styrene at 50°. With procedures A and B, 0.1 to 0.4 g. more of monomer was weighed into the reaction flask than was required to give an exactly 0.01 M solution of ABN, but the loss of monomer in the gas stream was such that the average monomer present (reacted and unreacted) was usually within 0.5% of that required to give the specified catalyst concentration. The yields were corrected to the calculated average volume of solution by allowing for all mechanical losses in transfer. The rates were obtained by dividing the moles of each product found by the average volume of the reaction mixture in liters and the reaction time in hours. No allowance was made for the slow decrease in concentration of ABN (8% in 7 hours),[9] or for any volume change due

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[7] R. H. Boundy and R. F. Boyer, "Styrene," Reinhold Publishing Corp., New York, N. Y., 1952, p. 55.

[8] W. Patnode and W. J. Scheiber, THIS JOURNAL, **61**, 3449 (1939).

[9] J. W. Breitenbach and A. Schindler, *Monatsh.*, **83**, 724 (1952), give the first-order rate constant for the decomposition of ABN in styrene at 50° as 0.0107/hr.

TABLE I

METHANOL-SOLUBLE AND METHANOL-INSOLUBLE FRACTIONS OF PRODUCTS 55-69

Expt.	O_2 pressure mm.	Insoluble fraction Wt., g.	Insoluble fraction C, %	Soluble fraction Wt., g.	Soluble fraction C, %	Average C, %
55	75.5	10.05	72.1	0.47	..[a]	72.1
56	26.0	6.67	72.3	0.66	69.4[a]	72.1
57	13.5	3.18	74.0	1.06	73.9	74.0
58	11.7	2.97	74.3	1.21	73.5	74.1
59	4.7	1.50	78.7	1.11	75.6	77.4
69	0.76	0.656[b]	83.0	0.40	80.7	82.2
		.486[b]	82.1			
68	.74	.94	82.2	.87	82.4	82.3
67	.44	1.43	82.4	.65	78.8	81.3

[a] This fraction is assumed to be $C_8H_8O_2$, with 70.6% C, in the calculations. [b] The insoluble polymer was precipitated in two fractions, which proved to have nearly the same average composition.

to absorption of oxygen, because most of the runs had similar reaction times.

In procedure C, calculations were based on the weight of reaction mixture transferred for low temperature distillation. To compensate at least partially for an increase in density during oxidation, the weight of peroxide oxygen found was subtracted from the weight of sample taken for analysis. The volume of the sample was then calculated directly from the density of pure styrene at 50°. Otherwise the same principles were used as are described for procedures A or B. When benzene was used as solvent, its density at 50° was taken to be 0.8454 and its vapor pressure, 269 mm. For mixtures with an equal volume of monomer, the densities and vapor pressures were simply averaged.

2.6. **Decomposition of Styrene Peroxide.**—Two experiments, O and P, were carried out with a 9.94% solution of styrene peroxide in α-methylstyrene. This peroxide was the methanol-insoluble fraction of a peroxide prepared at 1 atm. of oxygen. Benzaldehyde in distillates was determined[4] by the dinitrophenylhydrazine method, in residues by infrared. No epoxide was found in either experiment.

The object of decomposition O was to determine the products of the fast, high-temperature pyrolysis. Here, 44.56 g. of the solution above was heated quickly in a stream of nitrogen over a period of 12 minutes from 10° to incipient distillation (163°). Most of the decomposition took place in 2 minutes at 135-150°, as indicated by evolution of formaldehyde gas. Of the oxygen in the original peroxide, 75.3% was found as benzaldehyde and an assumed equivalent of formaldehyde, 14.8% was in 1.49 g. of a residue not volatile at 100° and 0.4 mm. (82.2% C, 7.51% H), and 10.3% was lost as unidentified volatile products. The infrared absorption of the residue showed the presence of α-hydroxyacetophenone, at least 6% and not over 20%, corresponding to 2-7% yield from the initial peroxide. Thus, of the original peroxide, about 75% depolymerized to aldehydes (less if some hydroxyacetophenone decomposed to aldehyde, more if some benzaldehyde reacted further) and at least 2% decomposed by the disproportionation mechanism.

The object of decomposition P was to determine the extent of depolymerization of polyperoxide at 50°. The styrene peroxide solution was sealed off in an evacuated Pyrex tube containing a thermometer and irradiated over a type 16200 Hanovia quartz mercury arc for 61 hours. The distance from the arc to the center of the peroxide solution was regulated to hold the liquid temperature near 50° and averaged about 10 cm. The liquid temperature limits were about 40 and 60°, and the temperature was between 48 and 52° for 42 of the 61 hours. No excess pressure was observed on opening the tube. Analysis of 66.3 g. of reaction mixture indicated that of the original oxygen, 28.1% remained as peroxide, 20.0% appeared as benzaldehyde (40.1% yield on the peroxide) and 42.2% as high-boiling residues. Very little paraformaldehyde appeared in the reaction mixture. By difference, 9.7% of the original oxygen was lost as formaldehyde gas during analysis, and about a quarter of the oxygen in the residue corresponded to bound or polymerized formaldehyde. In this experiment the peroxide remaining was estimated as equivalent to the additional benzaldehyde formed when the residue was pyrolyzed by heating to 150° at 15 mm. pressure. Thus, of the peroxide decomposed by photolysis, 56% was found as benzaldehyde (and presumably formaldehyde), the remainder as residues which may represent products either of disproportionation or of reaction of alkoxy radicals with α-methylstyrene, or both. No indication of α-hydroxyacetophenone was found, but this compound may not be stable under the conditions of the experiment.

2.7. **Investigation of Polyperoxides.**—Three fairly homogeneous polyperoxides were compared in oxygen content, oxidizing power and pyrolysis in an effort to obtain quantitative data on polymer structure, but only semi-quantitative conclusions could be drawn.

Polyperoxides 135, 129 and 132, made at oxygen pressures of 740, 15.3 and 1.1 mm., were precipitated from benzene with methanol. Small high-styrene fractions of 129 and 132, and methanol-soluble fractions from all three, were discarded. The precipitates were washed thoroughly with methanol and then freed from volatile matter as described for procedure B (section 2.2). The residues were analyzed for carbon and hydrogen, for peroxides by the thiocresol method,[5,10] and for yields of benzaldehyde on pyrolysis. In the pyrolysis experiments, 0.1-0.2 g. of peroxide was spread, as a benzene solution, over the wall of a test-tube, 15 mm. in diameter. The tube was then evacuated to 0.5 mm. pressure and the contents were pyrolyzed (to refluxing of the decomposition products in 129 and 132) by gentle heating with a gas flame.[5] The vapors evolved were collected in a trap cooled to −78°, and analyzed for benzaldehyde with dinitrophenylhydrazine.[4]

Results are summarized in Table II. Apparently neither the thiocresol method nor the benzaldehyde method is quite quantitative. In 135, the peroxide made at atmospheric pressure, benzaldehyde determinations indicate that 7-8% of the oxygen is in end groups or ether links, not as $-CH_2CH(C_6H_5)O_2-$ units. This result checks expt. 56 in paper II.[5] Since end groups contain relatively little hydroperoxide,[4] the thiocresol method apparently accounts for 94% of the peroxide and for 87% of the oxygen in this polymer. If the thiocresol method also accounts for 94% of the peroxide in the other polymers, then 79% of the oxygen in 129 is in peroxide units, 55% in 132, the remainder being in ether links or end groups. The benzaldehyde determinations show either that up to 50% of the $-CH_2CH(C_6H_5)O_2-$ units in these polymers fail to liberate benzaldehyde, or that there is a substantial proportion of another kind of peroxide unit.

TABLE II

ANALYSES OF POLYPEROXIDES

Polyperoxide No.	Polyperoxide Prepn., mm. O_2	Millimoles of oxygen or peroxide per g. polymer[a]: Oxygen by combustion	Peroxide by Thiocresol[e]	Peroxide by BzH[f]
135	740	7.22[b]	6.19, 6.35	6.61, 6.72
129	15.3	6.45[c]	4.77, 4.83	4.07, 3.95
132	1.1	4.28[d]	2.19, 2.23	1.19[g]

[a] Theoretical for $(C_8H_8O_2)_n$, 7.35. [b] 70.8, 70.7% C; 6.18, 6.11% H; 23.1% O by difference. [c] 73.1, 72.9% C; 6.27, 6.43% H; 20.65% O by difference. [d] 78.9, 79.3% C; 7.15, 7.18% H; 13.7% O by difference. [e] Assuming that one peroxide unit oxidizes two mercaptan groups. [f] Assuming that one molecule of benzaldehyde is liberated from every $-CH_2CH(C_6H_5)O_2-$ unit, but not from any other unit. [g] Value supported by duplicate run with known small mechanical loss.

3. Mechanisms, Equations and Definitions

Table III lists in one place the reactions required to account for the most significant results in this and the next four papers. M is a monomer unit, and M· and MO_2· are free radicals of unspecified length ending in monomer or peroxide units. In this paper, M· and MO_2· correspond to $\sim\sim CH_2$-

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(10) In the present work, with peroxides from both styrene and α-methylstyrene, more base (0.2 instead of 0.1 ml. of 0.5 *N* sodium methoxide), and a longer reaction time (10 min. instead of 2 min.) were used because somewhat more mercaptan was oxidized under these conditions with peroxide containing excess monomer.

TABLE III

REACTIONS IN THE OXIDATION OF UNSATURATED COMPOUNDS

$\text{Initiator} \longrightarrow 2\text{ radicals} \xrightarrow{\mathrm{M}} \mathrm{2M\cdot}$		Chain Initiation	(1a)
$\xrightarrow{\mathrm{O_2}} \mathrm{2MO_2\cdot}$			(1b)
$\mathrm{M\cdot + M \xrightarrow{k_p} M\cdot}$		Propagation reactions	(2)
$\mathrm{M\cdot + O_2 \xrightarrow{k_{po}} MO_2\cdot}$		for addition to	(3)
$\mathrm{MO_2\cdot + M \xrightarrow{k_{pm}} M\cdot}$		double bond	(4)
$\mathrm{2M\cdot \xrightarrow{k_{tm}}}$		Chain	(5)
$\mathrm{M\cdot + MO_2\cdot \xrightarrow{k_{tom}}}$	non-radical products	terminating	(6)
$\mathrm{2MO_2\cdot \xrightarrow{k_{to}}}$		reactions	(7)
$\mathrm{MO_2CH_2CRR'\cdot \xrightarrow{k_e} MO\cdot + H_2}\overbrace{\mathrm{C{-}C}}^{\mathrm{O}}\mathrm{RR'}$		Epoxidation	(8)
$\mathrm{MO(OCH_2CRR'O)_n\cdot \xrightarrow{k_{cd}} MO\cdot + \mathit{n}CH_2O + \mathit{n}RR'C{=}O}$		Cleavage by depolymerization	(9)
$\mathrm{R''OCH_2CRR'O\cdot \longrightarrow R''OCH_2\cdot + RR'C{=}O}$		Decomposition of	(9a)
$\mathrm{R''OCH_2\cdot \longrightarrow R''\cdot + CH_2O}$		terminal radicals	(9b)
$\mathrm{MO\cdot + M \xrightarrow{k_a} M\cdot}$		Addition of alkoxy radicals	(10)
$\mathrm{MO_2\cdot + H_2C{=}CRR' \xrightarrow{k_{ch}} M\cdot + CH_2O + RCOR'}$		High pressure	(11)
or		cleavage accompanying	
$\mathrm{MO_2M\cdot + O_2 \xrightarrow{k'_{oh}} MO_2\cdot + CH_2O + RCOR'}$		propagation	(12)
$\mathrm{MO_2CH_2CRR'O_2\cdot \xrightarrow{k_{chu}} MO_2\cdot + CH_2O + RCOR'}$		Unimolec. high press. cleavage	(13)
$\mathrm{2MO_2\cdot \xrightarrow{k_{chb}} 2MO\cdot + O_2}$		Bimolecular high press. cleavage	(14)
$\mathrm{A\cdot + O_2 \xrightarrow{k'_{pa}} AO_2\cdot}$		Propagation for	(15)
$\mathrm{AO_2\cdot + RR'C = CR''CH_2R''' \xrightarrow{k'_{pm}} AO_2H + RR'C = CR''\dot{C}HR'''(= A\cdot)}$		formation of hydroperoxide	(16)

$\mathrm{CH(C_6H_5)\cdot}$ and $\sim\mathrm{CH_2CH(C_6H_5)OO\cdot}$. Reactions 1 – 4 and 7 have been established[4] where the rate of oxidation is independent of oxygen pressure. Termination 6 will be shown to apply to styrene at oxygen pressures below 4 mm. and to α-methylstyrene at pressures below 50 mm. Reactions 1a, 2 and 5 represent most vinyl polymerizations in the absence of oxygen. Reactions 15 and 16 replace 3 and 4 for olefins with reactive hydrogen and unreactive double bonds.[11,12]

The remaining reactions in Table III, 8–14, result from our efforts to correlate our data. A major object of these papers is to justify these deductions. The most difficulty arises from reactions 9, 9a, and 9b: to what extent do the terminal MO radicals break up further by 9a and 9b before chain propagation is resumed? With styrene at low oxygen pressures, the terminal MO· in reaction 9 usually contains two successive monomer units, $\sim$MMO·. Reaction 9 is usually followed by addition of styrene (reaction 10), occasionally by reaction 9a. With α-methylstyrene at low pressures, the terminal MO· includes R″O·, where R″ is a stabilized radical (*cf.* section 8.5), and reaction 9b as well as 9a usually follows 9 directly, and is in turn succeeded by 2 or 3.

The kinetic expressions to be derived in this section assume: (A) that reactions of M· and $\mathrm{MO_2\cdot}$ depend only on their end groups; (B) that reactions 2, 3, 4 and 10 account for all the consumption of monomer and oxygen; (C) that reactions 9a and 9b can be neglected; and (D) that reactions 5–7 account for all chain termination. Assumption B implies that kinetic chains are long enough so that consumption of monomer and oxygen in reaction 1 may be neglected; B also implies that

$$k_{po}[\mathrm{M\cdot}][\mathrm{O_2}] = k_{pm}[\mathrm{MO_2\cdot}][\mathrm{M}] \qquad (17)$$

Assumptions B and D together imply that reaction 10, which may be either addition or hydrogen transfer, is the only reaction by which alkoxy radicals disappear, *i.e.*, that MO· radicals are so much more reactive than M· or $\mathrm{MO_2\cdot}$ radicals toward monomer that MO· radicals do not participate in termination. Reaction 8 is possible only for the fraction of monomer radicals with a penultimate peroxide group ($R_\mathrm{M}/R_\mathrm{O}$). Some modifications of these assumptions will be considered later.

Table IV is based on the scheme above. It shows the concentrations of M· and $\mathrm{MO_2\cdot}$ radicals, and the total rates of consumption of monomer and oxygen, when each of the termination mechanisms 5–7 is dominant. R_i is the rate of production of effective radicals from the initiator. In the general case, when more than one termination mechanism applies, R_i and the termination constants are defined by equation 18.

$$R_i = 2k_{tm}[\mathrm{M\cdot}]^2 + 2k_{tom}[\mathrm{M\cdot}][\mathrm{MO_2\cdot}] + 2k_{to}[\mathrm{MO_2\cdot}]^2 \qquad (18)$$

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(11) J. L. Bolland, *Quart. Revs.*, **3**, 1 (1949).

(12) L. Bateman, *ibid.*, **8**, 147 (1954).

TABLE IV

DEPENDENCE OF RADICAL CONCENTRATIONS AND REACTION RATES ON TERMINATION MECHANISM

Rate or concentration	Termination mechanism $2\mathrm{MO_2}\cdot \xrightarrow{k_{\mathrm{to}}} \mathrm{X}$ (7)	$\mathrm{MO_2}\cdot + \mathrm{M}\cdot \xrightarrow{k_{\mathrm{tom}}} \mathrm{X}$ (6)	$2\mathrm{M}\cdot \xrightarrow{k_{\mathrm{tm}}} \mathrm{X}$ (5)
$[\mathrm{MO_2}\cdot]$	$\left(\frac{R_i}{2k_{\mathrm{to}}}\right)^{1/2}$	$\left(\frac{k_{\mathrm{po}}[\mathrm{O_2}]R_i}{2k_{\mathrm{pm}}[\mathrm{M}]k_{\mathrm{tom}}}\right)^{1/2}$	$\frac{k_{\mathrm{po}}[\mathrm{O_2}]}{k_{\mathrm{pm}}[\mathrm{M}]}\left(\frac{R_i}{2k_{\mathrm{tm}}}\right)^{1/2}$
$[\mathrm{M}\cdot]$	$\frac{k_{\mathrm{pm}}[\mathrm{M}]}{k_{\mathrm{po}}[\mathrm{O_2}]}\left(\frac{R_i}{2k_{\mathrm{to}}}\right)^{1/2}$	$\left(\frac{k_{\mathrm{pm}}[\mathrm{M}]R_i}{2k_{\mathrm{po}}[\mathrm{O_2}]k_{\mathrm{tom}}}\right)^{1/2}$	$\left(\frac{R_i}{2k_{\mathrm{tm}}}\right)^{1/2}$
$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} (= R_{\mathrm{M}})$	$\frac{k_{\mathrm{pm}}[\mathrm{M}]}{k_{\mathrm{po}}[\mathrm{O_2}]}\left(\frac{R_i}{2k_{\mathrm{to}}}\right)^{1/2}(\mathrm{MOE})$	$\left(\frac{k_{\mathrm{pm}}[\mathrm{M}]R_i}{2k_{\mathrm{po}}[\mathrm{O_2}]k_{\mathrm{tom}}}\right)^{1/2}(\mathrm{MOE})$	$\left(\frac{R_i}{2k_{\mathrm{tm}}}\right)^{1/2}(\mathrm{MOE})$
		$(\mathrm{MOE}) = k_{\mathrm{p}}[\mathrm{M}] + k_{\mathrm{po}}[\mathrm{O_2}] + k_{\mathrm{e}}R_{\mathrm{O}}/R_{\mathrm{M}}$	
$\frac{-\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} (= R_{\mathrm{O}})$	$k_{\mathrm{pm}}[\mathrm{M}]\left(\frac{R_i}{2k_{\mathrm{to}}}\right)^{1/2}$	$\left(\frac{k_{\mathrm{pm}}[\mathrm{M}]k_{\mathrm{po}}[\mathrm{O_2}]R_i}{2k_{\mathrm{tom}}}\right)^{1/2}$	$k_{\mathrm{po}}[\mathrm{O_2}]\left(\frac{R_i}{2k_{\mathrm{tm}}}\right)^{1/2}$

The combined rates of reaction of monomer and oxygen are given by equation 19.[13]

$$R_M + R_O = \frac{(r_1[\mathrm{M}]^2 + 2[\mathrm{M}][\mathrm{O_2}] + R_O k_e[\mathrm{M}]/R_M k_{\mathrm{po}})R_i^{1/2}/\delta_M}{(r_1^2[\mathrm{M}^2] + 2\phi r_1[\mathrm{M}][\mathrm{O_2}]\xi_O/\delta_M + [\mathrm{O_2}]^2\xi_O^2/\delta_M^2)^{1/2}} \quad (19)$$

where $r_1 = k_p/k_{\mathrm{po}}$, $\delta_M = (2k_{\mathrm{tm}})^{1/2}/k_p$, $\xi_O = (2k_{\mathrm{to}})^{1/2}/k_{\mathrm{pm}}$, $\phi = k_{\mathrm{tom}}/2k_{\mathrm{tm}}^{1/2}k_{\mathrm{to}}^{1/2}$, and R_M and R_O are the rates of reaction of monomer and of oxygen. This equation is adapted from that of Burnett[14] for the rate of a copolymerization when one monomer does not polymerize, using Flory's definition of the termination constants and of ϕ[15] (the tendency toward crossed termination) and our nomenclature, and adding a term to allow for consumption of monomer by reaction 10. The general expressions for R_M and R_O alone are very similar: the first factor in the numerator is

$$(r_1[\mathrm{M}]^2 + [\mathrm{M}][\mathrm{O_2}] + R_O k_e[\mathrm{M}]/R_M k_{\mathrm{po}})$$

for R_M(19a) and simply $[\mathrm{M}][\mathrm{O_2}]$ for R_O (19b). If we neglect the k_e term, dividing 19a by 19b gives

$$R_M/R_O = r_1[\mathrm{M}]/[\mathrm{O_2}] + 1 \quad (20)$$

irrespective of the mechanism of chain termination. The same expression also follows from the copolymer composition equation when one monomer reactivity ratio is zero.[4,16] If the k_e term is included, then equation 20 is replaced by

$$(R_M - R_E)/R_O = r_1[\mathrm{M}]/[\mathrm{O_2}] + 1 \quad (21)$$

where $R_E = R_O k_e[\mathrm{M}\cdot]/R_M$ = rate of formation of epoxide.

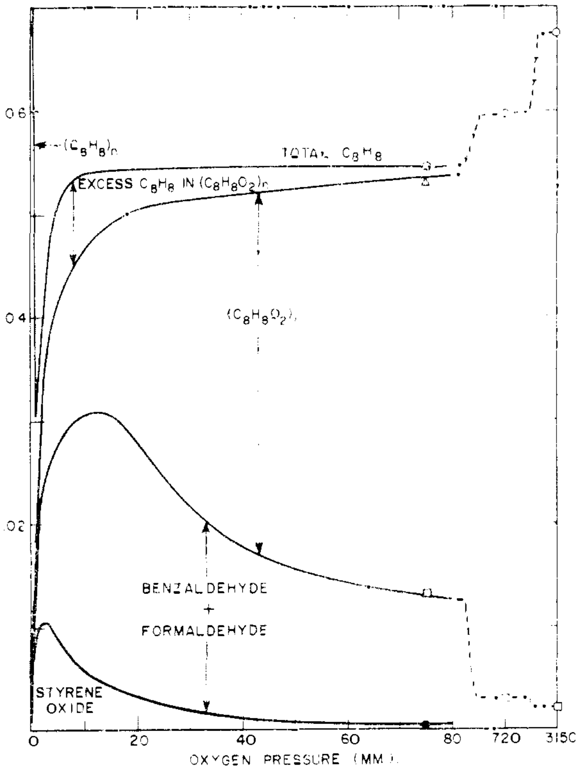

Fig. 1.—Rates and products of oxidation of styrene at 50° in presence of 0.01 *M* ABN. Only the mean value of the high-pressure points is shown since the reproducibility of these experiments is indicated in Fig. 7. Experimental points at pressures below 70 mm. are in Fig. 3.

4. Results and Discussion

4.1. Effect of Oxygen Pressure on Rate of Reaction.—Data on the rate and products of reaction of styrene at various oxygen pressures are presented in Table V and summarized in Fig. 1. Considering the different analytical methods employed, these rates agree well with those previously reported[4] for the range 25–730 mm. Figure 1 shows clearly the changes in termination mechanism, in the presence of 0.01 *M* ABN at 50°. In the absence of oxygen, styrene polymerizes to polystyrene at the rate of 0.095 mole/l./hr. Termination 5 has long been known to apply here. At oxygen pressures above 20 mm., the rate is nearly independent of oxygen pressure. The principal product is polyperoxide, and termination 7 has been established.[4] Between 0.5 and 1.0 mm. pressure of oxygen, the rate of reaction of styrene passes through a sharp minimum which is associated with termination 6. Figure 2 indicates that, over the range 0.5 to 4 mm. of oxygen, the rate of reaction of oxygen is nearly proportional to the square root of the oxygen pressure (line C), as required for termination 6 in Table IV. The oxygen line (C) corresponds to $R_O = 0.020\ p^{1/2}$ where p is the oxygen pressure in mm. From section 7.10, $[\mathrm{O_2}]$ in moles/l. is equal to 9.35×10^{-6}

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[13] The three terms in the factor in the numerator correspond to the relative contributions, respectively, of reaction 2, reactions 3 and 4 together, and reaction 10. The three terms in the denominator correspond similarly to terminations 5, 6 and 7.

[14] G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, Inc., New York, N. Y., 1954, p. 121.

[15] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 199, 200.

[16] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

TABLE V

THE AUTOXIDATION OF STYRENE WITH 0.01 M ABN[a] AT 50°

Expt.	Initial C_8H_8, g.	O_2 press., mm.	Moles O_2 Absorbed	Moles O_2 Exhausted	Reaction time, hr.	Rates in moles/l./hr. Excess C_8H_8	$(C_8H_8O_2)_n$	BzH (R_C)	C_8H_8O (R_E)	Total C_8H_8 (R_M)	Total O_2 (R_O)	C_8H_8/O_2 in total peroxide
64	35.12	0[b]	0	0	7.00	0.0948				0.0948	0.0	
107	131.9	0.19	.0015	0.0006	6.00	.0662	0.0012	0.0003	0.0004	.0681	.0017	50
67	131.8	0.44	.0172	.0012	6.00	.0117	.0081	.0063	.0090	.0351	.0189	2.28
68	131.8	.74	.0150	.031	6.05	.0102	.0069	.0056	.0082	.0309	.0166	2.54
69	131.8	.76	.0149	.0046	6.00	.0089	.0059	.0066	.0084	.0298	.0167	2.51
132[e]	88.0	1.1	.043	.026	7.00	.0197	.0215	.0242	.0261	.0915	.0587	1.91
80	131.8	1.74	.024	.026	6.06	.0079	.0100	.0122	.0093	.0394	.0268	1.78
83	131.8	2.9	.036	.0102	6.00	.0070	.0108	.0163	.0111	.0452	.0326	1.65
59	132.1	4.7	.039	.22	7.00	.0076	.0125	.0207	.0077	.0485	.0370	1.60
58	175.8	11.7	.065	.30	7.00	.0046	.0187	.0249	.0060	.0542	.0466	1.25
57[c]	175.7	13.5	.063	.23	7.00	.0045	.0186	.0236	.0067	.0534	.0455	1.25
129	131.8	15.3	.049	.097	7.00	.0036	.0199	.0239	.0058	.0532	.0467	1.18
130[e]	132.8	15.3	.103	.222	7.00	.0081	.0438	.0503	.0108	.1130	.0995	1.19
56	219.8	26.0	.088	.75	7.00	.0029	.0276	.0219	.0019	.0543	.0505	1.10
55	219.8	75.5	.096	.72	7.00	.0040	.0411	.0139	.0001	.0591	.0550	1.10
106	132.0	75	.049	.87	6.00	.0016	.0401	.0126	.0003	.0546	.0528	1.04
105	131.8	718	.054	.134	6.00		.0568	.0029		.0597	.0597	
C11	9.02	3140	.0020	None	3.00		.0652	.0017		.0669	.0669	
102	9.02	3150	.0014	None	2.00		.0653	.0023		.0676	.0676	
136	9.02	3150	.0013	None	2.00		.0627	.0029		.0656	.0656	
140	9.02	3190	.0016	None	2.50		.0637	.0020		.0657	.0657	
109[d]	4.51	3110	.0015	None	6.05		.0236	.0014		.0250	.0250	
139[d]	9.02	3280	.0019	None	4.00		.0228	.0009		.0237	.0237	
103[d,e]	9.02	3150	.0011	None	2.00		.0510	.0030		.0540	.0540	
142[e]	9.02	3100	.0014	None	1.00		.1366	.0041		.1407	.1407	
110[f]	18.1	3150	.00095	None	7.00		.0062	.0003		.0065	.0065	
138[f]	18.04	3170	.0019	None	16.00		.0057	.00008		.0058	.0058	
141[f]	18.04	3140	.0019	None	16.00		.0059	.00012		.0060	.0060	

[a] 2,2′-Azobis-(2-methylpropionitrile), *cf.* notes *e* and *f*. [b] Sealed, evacuated tube. [c] Stirred at 1000 r.p.m. instead of the usual 1500 r.p.m. [d] Contained equal volumes of benzene and styrene. [e] Contained 0.040 M ABN. [f] Contained no ABN.

p. From equation 19b, when all chains terminate by reaction 6

$$R_O = \left(\frac{[M][O_2]R_i}{2\phi r_1 \xi_O \delta_M}\right)^{1/2} = 0.020p^{1/2} \qquad (22)$$

Data are available to permit calculation of the crossed termination factor, ϕ, from equation 19 or 22, and then, in principle, the rates of reaction of styrene and oxygen over the whole pressure range. The primary difficulty is that r_1 is not known accurately and is not constant (section 4.5). Nevertheless, ϕ has been evaluated approximately: ϕ ranges from about 10 at high pressures up to at least 20 and perhaps 200 below 1 mm. pressure. This change partly compensates the accompanying change in r_1. Within the known variations and limits of r_1 and ϕ, equation 19 represents semiquantitatively the principal features of the rates of reaction of styrene and oxygen over a wide pressure range.

The above summary will now be justified. The discussion will show that while the value of ϕ depends on the expression chosen for r_1, ϕ is not a constant and ϕ must be larger at low pressures than at high pressures. The calculation of ϕ is a little complicated and requires information from succeeding sections. Some of the information required for application of equation 19 is in Table V, where rates are in moles/l./hr. and [M] = 8.43 M. From expt. 64, $R_M = R_i^{1/2}[M]/\delta_M = 0.0948$, and $R_i^{1/2}/\delta_M = 0.01124$. From the mean of expts. C11, 102, 136 and 140, $R_M = R_O = 0.0664 = R_i^{1/2}[M]/\xi_O$. Hence, $\xi_O/\delta_M = 1.43$. Section 4.5 shows that r_1 depends on what groups are attached to the terminal styrene radical [M·], and therefore on the oxygen pressure. The effective value of r_1 lies between the limits

$$r_1 = 1.8 \times 10^{-6}\,(p + 0.04)/(p + 1.6) \qquad (23)$$

and

$$r_1 = 3.3 \times 10^{-7}\,(p + 0.04)/(p + 0.3) \qquad (24)$$

The most probable relation is

$$r_1 = 8.9 \times 10^{-7}\,(p + 0.04)/(p + 0.8) \qquad (25)$$

Curve A-S in Fig. 2 corresponds to equation 19a with r_1 defined by equation 25, with $\phi = 12$, and with the k_e term equal to $10.6\,r_1[M]/(r_1[M]/[O_2] + 1)$. The k_e term is de-

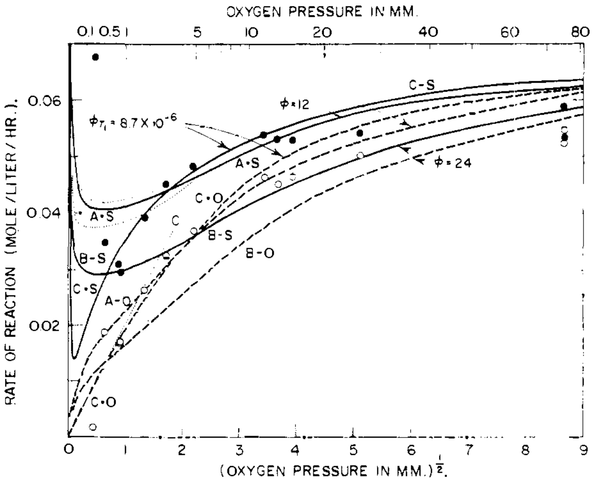

Fig. 2.—Rates of reaction of styrene (●) and oxygen (O) at 50° in presence of 0.01 M ABN.

rived in this way: $R_O/R_M = [O_2]/(r_1 [M] + [O_2])$ by equations 25 and 30; $k_e/k_{po} = k_e r_1/k_p = 16$ from equation 34. A factor of $^2/_3$ comes from the derivation of equation 30. The small proportion of methylene radicals from reaction 9a is considered to be equivalent to M· radicals. The value of ϕ is calculated from the above data and from R_M at 13.5 mm. (expt. 57 in Table V, chosen for the representative location of the R_M value in Fig. 2). The dotted variations of curve A-S near 1 mm. pressure represent possible errors in A-S corresponding to limiting values of r_1. The lower dotted curve assumes that the polymer contains one ether link for each epoxide formed. This curve is based on r_1 from equation 24, on $\phi = 26$ (again from expt. 57), and on the full average value of k_e/k_p, 25, from equation 35. The upper dotted curve neglects effects of ether links in the polymer and the k_e terms in equation 19a. This curve is based on r_1 from equation 28, and on $\phi = 6$ (from expt. 57). Inspection of the form of equation 19a and of the dotted forms of curve A-S show that the value chosen for r_1 is important for calculation of the rate of oxidation only in a narrow pressure range when the crossed termination reaction 6 is important. Even in this range, a wide variation in the choice of r_1 is possible, without much effect on the general shape of the R_M curve, provided that an appropriate value of ϕ is chosen. Therefore, an error in the choice of equation 25 to express the effective value of r_1 will produce a corresponding error in ϕ but will not affect the general shape of the R_M curve or our general conclusions.

Curve A-S in Fig. 2, with $\phi = 12$, has a broad minimum which does not fit the experimental values of R_M at 0.4–2 mm. pressure of oxygen. Curve B-S has the same basis as A-S except that $\phi = 24$ to fit the experimental points at 0.75 mm. Now the experimental points at other pressures fit curve B-S poorly, and the broad minimum persists. It is clear that no single value of ϕ in equation 19a will produce the required sharp minimum in R_M.

Rates of oxygen consumption, R_O, will now be considered. For curves A-O and B-O, corresponding to equation 19b, the r_1 and ϕ values are the same as for curves A-S and B-S, respectively. The employment of a constant ϕ and variable r_1 in each curve seems to preclude the proportionality between R_O and $[O_2]^{1/2}$ which is apparently required below 4 mm. pressure by the experimental points and by equation 22. When the substitution from equation 22, $\phi r_1 = 8.7 \times 10^{-6}$, is made in equation 19, then the A and B curves in Fig. 2 take the form of the C curves. The oxygen curve, C-O, has the correct form above 2 mm. pressure (where the ϕr_1 term becomes unimportant) and becomes a straight line below 2 mm. pressure (when over 80% of the termination from this calculation is by interaction of M· and MO_2· radicals).[13] The styrene curve, C-S, has the necessary sharp minimum, but at 0.01 mm. pressure of oxygen instead of at 0.75 mm. No reasonable error in any of the other experimental values in equation 19 seems responsible for the discrepancy. The most reasonable conclusion is that the concentration of oxygen in solution was not maintained at the recorded values when these were 2 mm. or less. In this event, curve C-S may represent the rate of reaction of styrene as well or better than the experimental points.

Since r_1 is undoubtedly changing over the pressure range shown in Fig. 2, ϕ must be changing also. Thus the change in radical structure from MO_2M· to MM· results in an increasing rate of reaction with MO_2· radicals[17] as well as with molecular oxygen (section 4.5), and apparently for the same reason. Changes in ϕ values with changes of proportions of monomers have been noted previously in copolymerizations.[18] These changes have been correlated with changes in the penultimate unit, but with the assumption that r_1 does *not* depend on the penultimate unit.[19,20] Section 5 indicates why the styrene–oxygen system is particularly suitable for studying changes in ϕ and r_1.

Curve C-O suggests that ϕr_1 is constant, and curve C-S suggests that effective oxygen concentrations were lower than the stated values in low-pressure experiments. These two suggestions are inconsistent. If we admit the error in oxygen concentrations, then a curve like A-O or B-O may describe oxygen rates better than the line C and the curve C-O, and ϕr_1 is no longer a constant. The best compromise seems to be that ϕ varies continuously with radical structure, like r_1, so that ϕr_1 decreases steadily with oxygen pressure, but not as rapidly as r_1. The maximum value of ϕ might then be around one-half of $8.7 \times 10^{-6}/r_1$ at the minimum value of r_1, $r = 4.4 \times 10^{-8}$; ϕ would then be about 100 rather than about 200. Either value is much greater than the high pressure value, about 10. Thus, the best representation of the rate of reaction of styrene, at oxygen pressures below 2 mm., would be a curve somewhere in between the present experimental points in Fig. 2 (which probably overstate the oxygen pressure) and curve C-S (which probably exaggerates the value of ϕ).

Finally, none of the curves fit the experimental points very well at oxygen pressures above 20 mm. Either the rates in the 26, 75 and 718 mm. experiments are too low (by up to 10%) for the 3200 mm. experiments, or else the latter are too fast and the value of ξ_O used in all the calculations is too small. Some extra contribution of high oxygen pressure to the rate of oxidation is suggested.

The last eleven experiments in Table V show the effects of thermal initiation, monomer concentration, and initiator concentration at 3100–3200 mm. pressure of oxygen. The rate of thermal oxidation is about one-tenth the rate of the oxidation initiated by 0.01 *M* ABN. The rate of initiation in the latter experiment is therefore about 100 times the rate of thermal initiation. Accordingly, the thermal initiation can be neglected in the presence of initiator and cannot be responsible for the observed slow increase in catalyzed rate with pressure above one atmosphere of oxygen.[21] The thermal rates in expts. 110, 138 and 141 agree satisfactorily with the 0.0057 mole/l./hr. predicted by the relation which applies over the pressure range 90–730 mm.,[4] $R_O = 0.15[M]^{1.38}[p]^{0.37}$.

The effect of ABN concentration on the rate of oxidation at 3200 mm. of oxygen is about the same as previously reported[4] at one atmosphere. Either in bulk (expts. C11, 102, 136, 140, 142), or in a 50% solution in benzene (expts. 109, 139, 103), the indicated rate is proportional to $[ABN]^{0.54}$ and $[ABN]^{0.56-0.59}$, respectively. At one atmosphere, the actual apparent exponent was 0.59. The effect of monomer concentration on rate of oxidation does not agree as well. With bromobenzene as diluent at one atmosphere, the rate was proportional to [M] within experimental error.[4] With benzene as diluent at 3200 mm. of oxygen, the rate is proportional to $M^{1.4-1.5}$. The significance of this discrepancy is uncertain.

4.2. The Retarding Effects of Oxygen on Polymerization.—The data in Table V and Figs. 1 and 2 provide, for the first time,[22] a clear description of the retarding effect of oxygen on the initiated polymerization of styrene. In solution polymerization, the retarding effect varies with pressure but is small. Oxygen is consumed nearly as fast as styrene, and with sufficient agitation, polymerizing styrene is a good scavenger for oxygen.[23] For styrene initially saturated with oxy-

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[17] The difference between MO_2MMO_2· and MO_2MO_2· is neglected because the change is separated from the free valence by four atoms.

[18] J. C. Bevington, H. W. Melville and R. P. Taylor, *J. Polymer Sci.*, **14**, 463 (1954).

[19] W. G. Barb, *ibid.*, **11**, 117 (1953).

[20] E. J. Arlman, *ibid.*, **17**, 375 (1955).

[21] Assuming that the ABN initiation is 100 times as fast as the thermal initiation, then the over-all rate of oxidation should be $\sqrt{101}$ times the thermal rate. The contribution of thermal initiation is thus about 0.5%.

[22] H. Trenne, *Chem. Ztg.*, **74**, 692 (1950), has stated that the rate of polymerization of styrene passes through a sharp minimum at an unspecified, very low, oxygen concentration. He reported aldehydes, but not polyperoxide, in the products.

[23] In expt. 107, an air–nitrogen mixture containing 6.2 mole % of

gen at 1 atm. and containing 0.01 M ABN, with no additional oxygen available, the reaction of styrene at 50° should proceed at an average rate of about half the normal rate of homopolymerization during the 10 minutes (about 2 minutes with air) while the oxygen is being consumed. The polymerization then proceeds at the normal rate, little affected by the peroxide present[4] at temperatures below 80°.

Henrici-Olivé and Olivé have recently reported[24] their dilatometric study of the effect of oxygen on the ABN-initiated polymerization of styrene at 50°. With benzene–styrene mixtures which were initially saturated with air or oxygen, they found induction periods proportional to [styrene][ABN]$^{1/2}$. During the induction period, the rate of volume change was 1/4 to 1/7 of the subsequent rate, but the formation of aldehydes and of copolymers of varying composition complicates the interpretation of their volumetric data. Our work supports their conclusion that $r_1 < 7 \times 10^{-5}$ (section 4.5) and that autocatalysis by polyperoxides is negligible in ABN-initiated polymerizations at 50°.[4] However, since they assumed that alternating polyperoxide is the sole polymer until all the oxygen is consumed, some of their other conclusions need further examination.[24a]

The thermal polymerization of styrene is mildly accelerated by oxygen. In the presence of one atmosphere of oxygen at 50° and in the absence of added initiators and solvents, the rate of reaction of styrene is 0.00347 mole/l./hr., three times the rate of polymerization in the absence of oxygen.[4] Thus the contribution of oxygen to thermal chain initiation[4] more than offsets the mild retarding effect of oxygen which is observed in initiated polymerizations. For thermal polymerizations, initially saturated with air or oxygen,[4] and without a vapor space, the initial acceleration should gradually disappear in about one-half or three hours, respectively. Sometime previously, Goldfinger and Lauterbach[25] arrived at qualitatively similar conclusions. They showed that oxygen slightly accelerates the thermal reaction of styrene until the oxygen is consumed. The thermal polymerization then proceeds normally.

Bovey and Kolthoff[26] report that oxygen reduces the rate of the emulsion polymerization of styrene to 0.12% of the rate in the absence of oxygen. The average rates of consumption of oxygen in their experiments at 50° were 0.09 to 0.24 mole/l./hr., calculated on the volume of styrene employed.[27] These rates are close to the rate, 0.06 mole/l./hr., reported in Table V for one atm. of oxygen and 0.01 M ABN. The reaction of styrene with oxygen in emulsion at 50° thus proceeds at the oil phase rate which would be expected at 0.02–0.2 M ABN. All these data on emulsion polymerization are consistent with the conclusion that oxygen prevents emulsion polymerization of styrene, or else removes most or all of the advantage of using an emulsion system, in either or both of two ways. (1) A water-soluble radical, such as $HO_2\cdot$ or $C_8H_7O_2\cdot$, may be produced by a chain transfer reaction which competes with the normal chain propagation. Some such process must occur because at least seven polyperoxide molecules are produced for each ABN molecule decomposed.[4] When escape of water-soluble radicals from emulsion particles becomes possible, then the radicals are no longer isolated from each other. They then combine in the aqueous phase and the advantage of emulsion polymerization is lost. (2) Because of higher water-solubility of short radicals such as $^-OSO_3(C_8H_8O_2)\cdot$ as compared with $^-OSO_3(C_8H_8)_n\cdot$, chain initiation in soap micelles and formation of emulsion particles may be relatively difficult in the presence of oxygen.

4.3. Effect of Oxygen Pressure on Products of Oxidation.—Paper I showed that styrene polyperoxide, benzaldehyde and formaldehyde are all primary products of oxidation.[4] The other major product, styrene oxide, is now assumed to be another primary product because it is formed only in traces in the decomposition of styrene polyperoxide (*cf.* section 4.4).[28]

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oxygen was introduced into the reaction flask at a constant gas pressure 15 mm. above the vapor pressure of styrene. The oxygen mixture was introduced at the rate of 0.0053 mole of total gas per hr. and the average contact time of the gas with the 0.15 l. of styrene was only 8–9 min. However, 79% of the available oxygen was removed, and its final pressure was reduced to 0.19 mm. in the exhausted gas. If equilibrium was not maintained between the liquid and vapor phases, polymerizing styrene is a better scavenger for oxygen than these figures indicate.

(24) G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **24**, 64 (1957).

(24a) ADDED IN PROOF.—Further consideration of the data in this paper and those of Henrici-Olivé and Olivé, and correspondence with them, has brought out the following points. There is good agreement on the rate of the oxygen-free polymerization. Their conclusion that the lengths of their induction periods were proportional to $(O_2)(M)^{-1}\cdot(ABN)^{-1/2}$ is consistent with our view that termination (7) predominated during most of the induction periods and that shorter contributions from termination (6) might not be detected (*cf.* Table IV). The two sets of data differ unaccountably in indicated rates of oxidation during the induction periods. Their rates of oxidation come from their estimated concentration of oxygen in styrene in equilibrium with air, 0.0010 M (0.0015 M from our Table VI) and the induction periods. These periods, measured dilatometrically in numerous experiments with freshly distilled styrene, extrapolate to about 5 min. for 0.01 M ABN. Under such conditions, their R_O = 0.012 mole/l./hr. Our values for R_O at 75–750 mm. pressure range from 0.053 to 0.060 mole/l./hr. (Table V and paper I), by analyses for polyperoxide and benzaldehyde. Integration of our equation 22 indicates that reaction of the last 5 mm. of oxygen would require about 2.6 times as long as reaction of the first 5 mm. (at 1 atm.), but such a retardation is far too small to account for the extended induction periods observed by them. Their recorded rates are probably not suitable measures of the propagation constant associated with alternation in copolymerization of styrene and oxygen or of the termination constant associated with reaction of two peroxide radicals. Considerations in footnote 67a also apply.

(25) G. Goldfinger and K. E. Lauterbach, *J. Polymer Sci.*, **3**, 145 (1948). This work employed a dilatometric technique and solutions saturated with air. The paper provides references to previous work, but since styrene polyperoxide is more soluble than polystyrene, precipitation procedures used by other workers to determine induction periods and rates are of limited value; *cf.* J. Abere, H. Mark and W. P. Hohenstein, *J. Appl. Chem. (London)*, **1**, 363 (1951).

(26) F. A. Bovey and I. M. Kolthoff, THIS JOURNAL, **69**, 2143 (1947).

(27) Initial styrene is reported[26] in "parts"; oxygen consumption is reported in mg., and the relation is not always clear. The calculations above refer to the high-speed shaking apparatus and are based on 5 g. of styrene for the first experiment described in the text on p. 2148, 5 and 10 g. for runs 1 and 2 in Table III. These rates are supported by an experiment in this Laboratory where an emulsion polymerization of 10 g. of styrene, 90 g. of water, 2.5 g. of Ivory soap and 0.3 g. of potassium persulfate under one atm. of oxygen absorbed oxygen at a rate of 0.079 mole/l. styrene/hr. over the first 6.5 hr.

(28) The possibility that styrene oxide results from the action of perbenzoic acid (formed from benzaldehyde) on styrene has been considered and rejected. Neither benzoic nor perbenzoic acid has been observed in infrared spectra of methanol-soluble peroxide obtained by procedure A or of peroxide obtained by procedure B, certainly not in

As the oxygen pressure decreases, maxima appear below 20 mm. pressure in the rates of formation of aldehydes and of styrene oxide, and the polymer changes from polyperoxide to polystyrene. Yields of formaldehyde are not shown because the assumption that this aldehyde and benzaldehyde are formed in equal quantities seems as useful as the analyses.[29] Since the elementary composition of the non-volatile residues of the oxidation is known, but the disposition of the oxygen is not, two methods have been used in representing our data. In Table V and in Fig. 1, the data are based on analyses of polymers for carbon and hydrogen and are presented as if the polymer contained only $-C_8H_8-$ and $-O_2-$ units. In Fig. 3, the data are presented as if the polymer contained one ether link (formed by reaction 10) for each molecule of styrene oxide formed (by reaction 8, without regard for reaction 9). To construct Fig. 3 from Table V, the rate of formation of ether links was set equal to the rate of formation of epoxide, R_E, and the rates of incorporation of "excess C_8H_8" and of "$(C_8H_8O_2)$" in Table V have both been reduced by $R_E/2$. This correction will be discussed in section 4.5. Figure 1 shows the total rate of consumption of styrene as the sum of the individual reactions. Figure 3 presents in a different manner the same data for the low pressure region. Each line (except the one for "total") shows the rate of formation of a single product, instead of a cumulative total as in Fig. 1. The experimental points are shown so that the reproducibility of the data can be gauged.

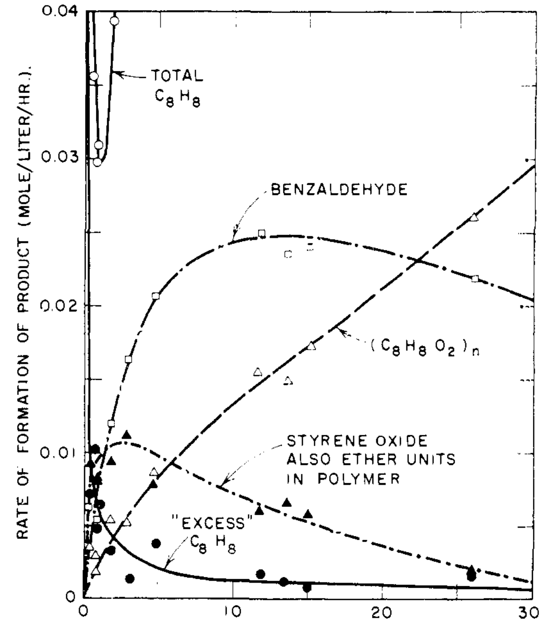

Fig. 3.—Rates and products of oxidation of styrene at 50° in presence of 0.01 *M* ABN.

In the succeeding sections, all the oxidation products of styrene will be accounted for by reactions 1–7, already discussed, and the additional reactions 8–12. The copolymerization of styrene and oxygen (reactions 3 and 4) is exothermic and apparently irreversible. Section 4.4 will show that the copolymer is nevertheless unstable: once a peroxide link is broken into two alkoxy radicals, each can depolymerize rapidly and exothermically into benzaldehyde and formaldehyde. This depolymerization may continue until the alternation of styrene and oxygen units is interrupted by an end group or by some irregularity in the chain. A discussion of chain irregularities (section 4.5 on polymer composition) follows. Section 4.6 shows how epoxide and cleavage products are formed from growing oxidation chains. As the life of radicals ending in monomer units (M·) becomes longer at low oxygen pressures, an increasing proportion of these radicals undergoes reaction (8) to give alkoxy radicals. The latter then rapidly depolymerize to cleavage products by reaction (9). A different cleavage mechanism (11 or 12) is required to account for a minor proportion of cleavage at high oxygen pressures. Introduction of reaction 9 for cleavage alters some earlier conclusions.[4,5]

4.4. Decomposition of Styrene Peroxide.—Decompositions of polyperoxides by heat or light yield carbonyl compounds which are also direct products of oxidation of the corresponding monomers. Decomposition and cleavage by direct oxidation seem to have the same intermediate, $RO(OCH_2CH(C_6H_5)O)_n\cdot$ with styrene peroxide, which depolymerizes to benzaldehyde, formaldehyde and a terminal radical. To help determine the course of the oxidation of styrene, we would like to know how far this depolymerization proceeds in styrene as solvent at 50°. An answer has been sought in the photolysis and pyrolysis of styrene polyperoxide. Both decompositions are assumed to produce the same intermediate alkoxy radicals, at 50° and below in photolysis, at higher temperatures in the dark. Only a partial answer has been obtained because of complications in the decomposition of styrene peroxide. (1) The decomposition in styrene as solvent causes polymerization of the monomer, making analyses more difficult. This difficulty was met by substituting α-methylstyrene for styrene as solvent. The methyl derivative has nearly the same ability to trap free radicals[16] but is not polymerized (section 8.1). (2) Styrene peroxide decomposes by *disproportionation* as well as by the depolymerization *chain* mechanism. Disproportionation results in gradual conversion of peroxide groups to hydroxyl and carbonyl groups, and ultimately in the formation of α-hydroxyacetophenone. (3) Although the yields of hydroxyacetophenone and benzaldehyde are measures of the two mechanisms of decomposition, both products are subject to secondary reactions of unknown importance. Data on the decomposition of styrene

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quantities comparable to epoxide formed. Further, the maximum rate of formation of epoxide does not coincide with the maximum rate of formation of benzaldehyde. Finally, such a process is not admissible for the formation of epoxide from α-methylstyrene.

(29) 78–83% as much formaldehyde as benzaldehyde was found in expts. 57–59, 58% in expt. 56, 42–48% in expts. 67–68 and 80, only about 30% in expts. 83 and 107. Formaldehyde was not determined in other experiments in Table V. The formaldehyde found was closest to the benzaldehyde found in the experiments where the latter aldehyde was formed in largest quantities. Some formaldehyde was lost or not accounted for as polymer in the reaction mixture and parts of the exhaust system.

peroxide show that some depolymerization of β-peroxyalkoxy radicals occurs in monomer as solvent, that complete depolymerization is neither excluded nor required, and that this depolymerization takes place less readily than with α-methylstyrene peroxide.

These conclusions are based on paper II,[5] and on expts. O and P in section 2.6. Decomposition of styrene peroxide to benzaldehyde proceeds by a radical chain mechanism. Because the photolysis is strongly retarded by hydroquinone or styrene,[30] chains are long in benzene solution at 25 and 50°. At 100°, the retarding effect of α-methylstyrene as solvent is less marked. Over the whole temperature range, up to one-third as much hydroxyacetophenone as benzaldehyde has been found, in both the presence and absence of retarders for the chain decomposition. In the photolysis of styrene peroxide in α-methylstyrene at 50° (expt. P), 56% of the peroxide decomposed was found as benzaldehyde (and an assumed equivalent of formaldehyde), the remainder as unidentified high-boiling materials. Since some peroxide decomposed by the disproportionation mechanism and since some benzaldehyde may have been lost by photolysis, complete depolymerization of every alkoxy radical is a possibility.[31] Thermal decomposition of some of the same peroxide solution near 140° (expt. O) gave 75% yield of benzaldehyde, but 2-7% of hydroxyacetophenone also was identified. The improved yield of benzaldehyde at the higher temperature suggests that even more benzaldehyde might have been found at 50° in the absence of disproportionation of peroxide and of secondary reactions of benzaldehyde. Here, we assume that an alkoxy radical requires more activation energy for addition to a double bond than for depolymerization.

Although β-peroxyalkoxy radicals from styrene peroxide can depolymerize by the chain mechanism, this reaction takes place less readily than with α-methylstyrene peroxide. The apparent activation energy for the formation of benzaldehyde in the early stage of photodecomposition in benzene is about 5 kcal./mole (Fig. 2 in paper II).[30] Photodecomposition without much depolymerization at −75° also suggests that a significant activation energy is required for depolymerization. On the other hand, section 8.3 shows that photodecomposition of α-methylstyrene peroxide requires little or no activation energy and that the chain decomposition of a single polyperoxide molecule (at or above 75°) is usually complete, even in α-methylstyrene as solvent. In photolyses at 25–50°, the corresponding monomer as solvent, or 0.5 *M* hydroquinone in benzene as solvent, is 4–10 times as effective in retarding the decomposition of styrene peroxide as in retarding α-methylstyrene peroxide, again suggesting that the depolymerization of styrene peroxide is slower and more easily interrupted. The observation that thiophenol retards photolysis of α-methylstyrene peroxide but not of styrene peroxide is given little weight because the effects of thiophenol vary with reaction time.

4.5. Composition of Copolymer.—The possibilities of formation of epoxide (reaction 8) and cleavage products (reaction 9) depend on the proportion of excess styrene in the polyperoxide and therefore on the oxygen pressure. Although an exact relation between the composition of a polyperoxide and the oxygen pressure during its preparation is obviously desirable, development of such a relation has proved to be complicated. The first complication is that the reactivities of the radicals involved depend on their penultimate units. The second complication is that the polymers do not contain only monomer and peroxide units, as assumed in Table V; they also contain ether (–O–) and methylene (–CH₂–) units and the proportions of these are not well known. This section considers the errors which may arise from ether and methylene units, presents limits on composition-pressure relations, and finally presents a most probable relation as a basis for other discussions. This section shows that the uncertainties in polymer composition have no effect on the qualitative conclusions of this paper, and a relatively minor effect on the quantitative conclusions.

The previous report of the oxidation of styrene[4] employed only the monomer:oxygen ratio in the polyperoxide to calculate r_1 by equation 20. However, the present paper shows that all the styrene and oxygen which appear as epoxide and aldehydes are also consumed by reactions 2-4. For determination of r_1, equation 20 is put in the form

$$\frac{R_M}{R_O} - 1 = \frac{8.43 r_1}{9.35 \times 10^{-6} p} = \frac{9.0 \times 10^5 r_1}{p} \qquad (26)$$

where 8.43 is the molar concentration of styrene at 50° and $9.35 \times 10^{-6} p$ is the molar concentration of oxygen at p mm. pressure of oxygen (section 7.10). A plot of $(R_M/R_O) - 1$ against $1/p$ should give a straight line with zero intercept and a slope $9.0 \times 10^5 r_1$. The solid circles in Fig. 4 show that r_1 is not constant and that its apparent value decreases as the oxygen pressure decreases and as the styrene content of the polymer (and growing radical) increases.

This relation is analogous to those observed in the copolymerizations of fumaronitrile,[19,32a] acrylonitrile,[32b] vinylidene cyanide[32c] or maleic anhydride[19] and in chain transfer reactions of carbon tetrachloride.[33,34] In these instances also, the tendency of the terminal hydrocarbon radical to react with nitrile, maleic anhydride or carbon tetrachloride, instead of more hydrocarbon, increased as the hydrocarbon content of the polymer radical increased. The equation of Barb[19] may be adapted to the oxidation of styrene and the present nomenclature

$$\frac{R_M}{R_O} - 1 = \frac{r'[C_8H_8]}{[O_2]} \times \frac{1 + r[C_8H_8]/[O_2]}{1 + r'[C_8H_8]/[O_2]} = \frac{9 \times 10^5 r'}{p} \times \frac{p + 9 \times 10^5 r}{p + 9 \times 10^5 r'} \qquad (27)$$

Here, $r = k_p/k_{po}$ for a radical with a penultimate styrene unit (MM·), and $r' = k_p/k_{po}$ for a radical with a penultimate peroxide unit (MO₂M·).[35] The upper curve in Fig. 4 corresponds to equation 28 and to $r = 4.4 \times 10^{-8}$ and $r' = 1.8 \times 10^{-6}$ in equation 27.

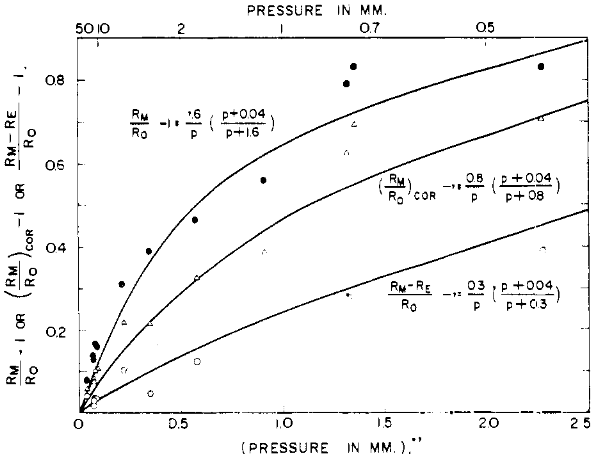

Fig. 4.—Relative rates of reaction of styrene (R_M) and oxygen (R_O) at 50° as a function of oxygen pressure.

$$\frac{R_M}{R_O} - 1 = \frac{1.6}{p} \times \frac{p + 0.04}{p \times 1.6} \qquad (28)$$

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[30] The ordinate in Fig. 2 in paper II is in error; all concentrations of benzaldehyde are in *tenths* of a mole/liter.

[31] This conclusion supersedes some of the discussion in paper II.

[32] (a) R. G. Fordyce and G. E. Ham, THIS JOURNAL, **73**, 1186 (1951); (b) G. E. Ham, *J. Polymer Sci.*, **14**, 87 (1954); (c) G. E. Ham, *ibid.*, **24**, 349 (1957).

[33] F. R. Mayo, THIS JOURNAL, **70**, 3689 (1948).

[34] F. M. Lewis and F. R. Mayo, *ibid.*, **76**, 457 (1954).

[35] From equation 27, the *effective value* of r_1 in equation 26 is $r'(p + 9 \times 10^5 r)/(p + 9 \times 10^5 r')$. This concept will be used in other discussions.

The value for r' is somewhat smaller (as should be expected) than the value of r_1 in paper I,[4] 4×10^{-6}, but the two sets of data are entirely consistent when calculated on the same basis. The experimental errors and curve fitting method are such that r may well be in error by 50% and r' by 20%. Ratios for radicals ending in more than two consecutive monomer units cannot be obtained from the present data.

Equation 28 will be used as the upper limit R_M/R_O as a function of oxygen pressure. This equation assumes that the polymers, as reported in Table V and Fig. 1, contain only $-C_8H_8-$ and $-O_2-$ units in various proportions. We shall now consider an approach which gives the lower limit of R_M/R_O. We assume that for every molecule of epoxide formed by reaction (8) one alkoxy radical (MO·) is formed, and that every terminal alkoxy adds to monomer by reaction 10, regardless of the extent of depolymerization by reaction 9, to give one ether link in the final polymer. Decomposition of alkoxy radicals by reactions 9a and 9b is neglected. Figure 3 presents the data in Table V on this basis. The open circles in Fig. 4 show that equation 21 fails to give the linear plot corresponding to a unique value of r_1. This failure is not obvious in Fig. 4, but the line which accounts for the four experiments at 11–16 mm. cannot possibly accommodate any of the points below 3 mm. pressure. Equation 21 has therefore been put in a form like equation 27. The lowest line in Fig. 4 corresponds to equation 29, to $r = 4.4 \times 10^{-8}$ and $r' = 3.3 \times 10^{-7}$

$$\frac{R_M - R_E}{R_O} - 1 = \frac{0.3}{p} \times \frac{p + 0.04}{p + 0.3} \qquad (29)$$

The points scatter more than in the plot of equation 28 because R_E is known less accurately than any other rate and because the proportion of epoxide is nearly as large as the proportion of "excess" styrene in the copolymer. The value of r' is based on the points at 11–16 mm. pressure and may be in error by up to 30%. The value of r is so uncertain that we know only that it is considerably less than r'. The value chosen corresponds to that used in equations 27 and 28 because the difference between the two limiting expressions should disappear at very low pressures.

Whether we use the values of r and r' from equations 27–28 or from equation 29, we find that r (for MM· radicals) is around $4\text{–}5 \times 10^{-8}$ and that r' is 7–40 times as large. The direction of this change is such that it may arise either from an increasing tendency of $MO_2M_n\cdot$ to react with oxygen or a decreasing tendency to react with more styrene, as n increases from 1 to 2. Previous work with carbon tetrachloride,[33,34] nitriles[32] and maleic anhydride[19] has ascribed similar changes to resonance or electrostatic effects on the former tendency, but a steric effect on the latter tendency is possible in copolymerizations.[36] The difference between r and r' is not due to failure to keep the reaction mixture saturated with oxygen at low pressures: the change corresponds to relatively *increasing* reactivity of oxygen as the recorded oxygen pressure decreases to 0.44 mm. If the recorded pressures below 2 mm. are too high, as suggested in section 4.1, this correction would result in moving the low pressure points farther to the right in Fig. 4, in some smoothing of the curves, and in yielding still lower values for r. In expt. 107, at 0.19 mm. pressure, the high proportion of monomer in the product supports the suggestion that here an equilibrium concentration of oxygen was not maintained.

We shall now consider the relative merits of the limiting equations 28 and 29. The discussion will show first that there is ample evidence for both ether links and peroxide links in polyperoxide, but that there are probably not as many ether links as assumed in the development of equation 29. The discussion will then show that equation 28, which apparently ignores either links, is actually partially compensated for them.

Evidence for ether links comes from infrared spectra, peroxide determinations, and formaldehyde balances. First, infrared absorption spectra of methanol-insoluble or total non-volatile fractions from oxidations show that polyperoxides made at 0.5 to 50 mm. pressure of oxygen (particularly near the low end of this range) contain an absorption band at 9.10 μ which is absent in both high-pressure peroxide and in polystyrene. As this band increases in intensity in a series of polymers, the strong band of the high-pressure peroxide at 9.8 μ decreases in intensity. The two bands become of equal intensity near 1 mm. pressure. Both are presumably due to carbon–oxygen single bonds. No marked absorption due to hydroxyl or carbonyl is evident.

Quantitative evidence for ether links and equation 29 comes from analyses of polyperoxides by the thiocresol method. The derivation of equation 29 from 21 implies a correction of Table V, as indicated for Fig. 3 in section 4.3. Section 2.7 and Table II show that only 50–80% of the oxygen in polymers 129 and 132 was present in peroxide units. Most of the remainder was presumably in ether links. The results are complicated by end groups and the apparent inefficiency of the thiocresol method, but in expt. 129 the fraction of oxygen found as peroxide is very close to that calculated from Table V, as corrected for one ether link per molecule of epoxide. On the other hand, polymer 132 was found to contain about twice as much peroxide and about two-thirds as much ether as calculated from Table V (corrected). Thus, the derivation of equation 29 seems to overestimate the amount of ether in the polymer.

Formaldehyde balances show that in two experiments at least 60% of the terminal $RCH_2CH(C_6H_5)O\cdot$ or $RO_2CH_2CH(C_6H_5)O\cdot$ radicals do not split out benzaldehyde unless they also split out formaldehyde. Therefore, with at least 60% of the occurrences of reaction 8 an ether link should appear in the polymer. In both expts. 67–68, although formaldehyde equivalent to only 45% of the benzaldehyde was found,[29] the missing formaldehyde corresponds to only 38–39% of the styrene oxide found. Hence, at least 60% of the alkoxy radicals became ether links. In expt. 59, 80% as much formaldehyde as benzaldehyde was found.[29] Here the missing formaldehyde corresponds to slightly less than half the styrene oxide formed and at least 47% of the expected ether links should be present. Since analyses for formaldehyde are thought to be low,[29] the ether contents of the polyperoxides should be higher than the values given above.

Several kinds of evidence indicate that residual alkoxy groups from the depolymerization of styrene peroxide may decompose. Such decomposition is extensive with α-methylstyrene peroxide. Section 8.5 shows that about 80% of the residual MO· units decomposed to acetophenone (reaction 9a). Further, Table II showed that polymers 129 and 132 contained peroxide groups which could not yield benzaldehyde on pyrolysis. If most residual MMO· radicals decompose to $MCH_2\cdot$ and benzaldehyde at 150–200° *in vacuo*, then the peroxide analyses indicate the presence of peroxide groups other than $-MO_2-$, presumably $-CH_2O_2-$ from reaction of $MCH_2\cdot$ with oxygen. Lastly, section 4.6 and Fig. 6 indicate that depolymerization gives more benzaldehyde than would be expected if all depolymerization stopped at the residual alkoxy group.

Let us therefore consider the consequences of assuming that *all* terminal alkoxy groups (MMO· with styrene) decompose to $MCH_2\cdot$ and benzaldehyde, and that the terminal alkyl group then acts like an M· group in undergoing reactions with monomer and oxygen (reactions 2 and 3). It then follows that the R_O values in Table V are too high by $R_E/2$ (representing formaldehyde which was assumed to have been liberated) and the R_M values are too high by $R_E/8$ (representing $-CH_2-$ units in the polymer which were calculated from carbon analyses to be styrene). The net effect of these corrections is to increase $(R_M/R_O) - 1$ by about 37% (at 15 mm.) to 63% (0.4 to 0.8 mm.) and to increase the apparent values of r_1, r' and r similarly. Thus, the $(R_M/R_O) - 1$ curve in Fig. 4 lies about 30% below the curve

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[36] Scale models show that a polystyrene chain has rather closely packed substituents, and that poly-α-methylstyrene can be constructed only with difficulty. Since insertion of a peroxide link between monomer units greatly relieves the crowding, we might expect a reduced tendency of $M_n\cdot$ to react with monomer, as n increases.

which would correspond to complete decomposition of MMO· radicals and complete retention of residual potential formaldehyde units.[37]

Several considerations in this section suggest that after depolymerization by reaction 9, 60–70% of the residual MMO· radicals react with styrene by reaction 10 and that the remainder lose benzaldehyde to give $MCH_2\cdot$ radicals which then react with either styrene or oxygen. On this basis, for the calculation of r_1, r and r' in Fig. 4, the corrected R_M/R_O to be used is the average of 60–70% $(R_M - R_E)/R_O$ and 30–40% $(R_M - R_E/8)/(R_O - R_E/2)$. Accordingly, the corrected values, $(R_M/R_O)_{cor}$, used for the triangles and middle curve in Fig. 4 represent the sum of $^2/_3$ of the $(R_M - R_E)/R_O$ values and $^1/_3$ of the corresponding $(R_M - R_E/8)/(R_O - R_E/2)$ values. This curve is represented by equation 30 and corresponds to $r = 4.4 \times 10^{-8}$ and $r' = 8.9 \times 10^{-7}$.

$$\left(\frac{R_M}{R_O}\right)_{cor} - 1 = \frac{0.8}{p} \times \frac{p + 0.04}{p + 0.8} \qquad (30)$$

This average of R_M/R_O and these values of r and r' will be used as the most probable values for calculations in other sections. Values from equations 28–29 represent generous limits for these quantities.

4.6. Epoxidation and Cleavage.—Development of mechanisms for epoxidation and cleavage is based on three experimental considerations. (A) Figures 1 and 3 show that the rates and proportions of both reactions increase (up to the maxima) as the oxygen pressure decreases. Both must therefore be related to monomer radicals (M·), the only known reactant of which the concentration increases at low oxygen pressure. (B) The fraction of reacting oxygen appearing as cleavage products is closely proportional to (oxygen pressure)$^{-1}$ down to 50 mm. pressure. A small fraction of cleavage (2–3%) apparently will persist at very high pressures and therefore does not involve M· (except perhaps as a reaction with oxygen, as in reaction 12). (C) The ratio of the rates of cleavage and epoxidation, R_C/R_E, is a simple, nearly linear, function of oxygen pressure over the whole range where R_E is known with any accuracy, 0–26 mm. Since this range includes oxygen pressures at which both R_C and R_E pass through different maxima and at which three termination mechanisms apply, and includes experiments at both 0.01 and 0.04 *M* ABN, this relation is of special significance. It suggests that if pressure-dependent cleavage depends on $[O_2]^{-1}$, as found near 1 atm. of oxygen, then R_E is proportional to $[O_2]^{-2}$. One interpretation of these results is that R_C is first order in (M·) and that R_E is second order in (M·). This possibility was excluded because no plausible chain reaction could be found in which 2M· could react repeatedly to give 50–100 moles of epoxide per termination step or per ABN decomposed, and because R_C/R_E is independent of initiator concentration near both 1 and 15 mm. pressure of oxygen. On the other hand, the mechanism represented by reactions 8 and 9 is consistent with all the data. According to this scheme, epoxide arises from M·, which has the longest life at the lowest oxygen pressure. Cleavage may then follow formation of epoxide, but the extent of cleavage is limited by irregularities in the growing radical, and limited most at the lowest oxygen pressure.

The discussion below will show: (A) that R_E is consistent with reaction 8 and the over-all rate of oxidation when corrections are introduced for irregularities in the growing chains, (B) that R_C/R_E at low oxygen pressures can be correlated with chain irregularities, and (C) that cleavage at higher pressures apparently follows epoxide formation, even though epoxide formation is here too small to observe.

In relating R_E to equation 8 and irregularities in polymer structure, we shall consider R_E/R_O instead of R_E alone, to avoid complications due to changes in initiator concentration and in mechanism of chain termination.

$$\frac{R_E}{R_O} = \frac{k_e[M\cdot]}{k_{po}[M\cdot][O_2]} \times \frac{R_O}{R_M} = \frac{R_O}{R_M} \times \frac{k_e}{9.35 \times 10^{-6} p k_{po}} \qquad (31)$$

Equation 31 assumes the simplest rate expressions for reactions 8 and 3 and postulates that the fraction of monomer radicals which contain a penultimate peroxide link, and are therefore capable of undergoing reaction 8, is R_O/R_M. In the over-all reactions of monomer and oxygen at the growing chain ends, every absorption of oxygen is followed by reaction with monomer, permitting immediate formation of epoxide, but no other reactions which absorb M permit formation of epoxide. Equation 31 has been put in the form

$$\frac{R_E R_M}{R_O^2} = \frac{k_e}{9.35 \times 10^{-6} p k_{po}} \qquad (32)$$

for plotting in Fig. 5. The lowest set of points does not fall on the suggested straight line, but on a curve which is probably smooth within experimental error. The indicated value of $k_e/9.35 \times 10^{-6} k_{po}$ decreases from about 2 at oxygen

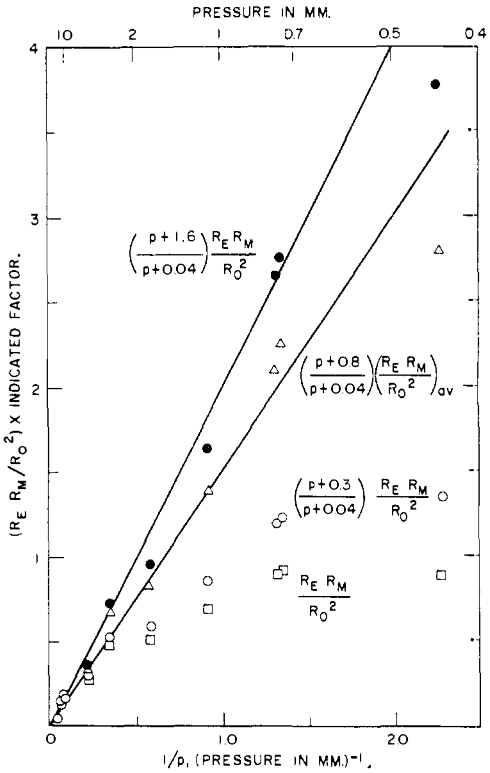

Fig. 5.—Relative rates of epoxidation (R_E) and total oxidation (R_O) of styrene at 50° as a function of oxygen pressure.

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[37] A distinction between styrene and α-methylstyrene, with respect to retention of formaldehyde units, is indicated in section 3.

pressures above 10 mm. to about 0.7 at 0.75 mm. pressure.[38]

The change by a factor of three in the apparent k_e/k_{po} ratio as the monomer content of the polymer increases is probably due mostly to change in k_{po}, established in section 4.5. If the change were instead in k_e, then any effect of excess M in a $RMO_2M\cdot$ radical would have to be transmitted past six atoms beyond R, since the R_M/R_O term in equation 30 allows for a penultimate monomer unit. Since, by definition, $k_{po} = k_p/r_1$, and since the effective value of r_1 at any pressure may be represented by equations 25 and 30, k_e can now be evaluated. Three relations are considered, of which 34 is the preferred relation and 33 and 35 indicate limits of errors.

$$\frac{p + 1.6}{p + 0.04} \times \frac{R_E R_M}{R_O^2} = \frac{0.19 k_e}{p k_p} = \frac{2}{p} \tag{33}$$

$$\frac{p + 0.8}{p + 0.04} \times \left(\frac{R_E R_M}{R_O^2}\right)_{av} = \frac{0.095 k_e}{p k_p} = \frac{1.5}{p} \tag{34}$$

$$\frac{p + 0.3}{p + 0.04} \times \frac{R_E R_M}{R_O^2} = \frac{0.036 k_e}{p k_p} = \frac{\sim 0.9}{p} \tag{35}$$

Equations 33 and 35 are based on R_M and R_O values in Table V and on the two limiting values of r_1 from equations 23 and 24, respectively. Equation 33 uses R_M and R_O values from Table V which have been corrected for loss of benzaldehyde from one-third of the alkoxy radicals, and the corresponding preferred values of r_1 from equation 25. Equations 33 and 34 give the expected linear plots with slopes of 2.0 and 1.5. These relations suggest that both k_e and k_p are independent of radical structure or that they undergo similar changes. Equation 35 gives a curve, apparently due to overcorrection for ether links in equation 24. The recorded "slope" for this curve, 0.9, corresponds to the slope of a line through the origin and the two points at 0.75 mm. pressure, when the error due to ether links should be small. The preferred value for k_e/k_p from equation 34 is 16, and the limiting values (11 and 25) are not greatly different. Since k_p = 123 mole/l./sec.,[39] k_e = 2000 sec.$^{-1}$.

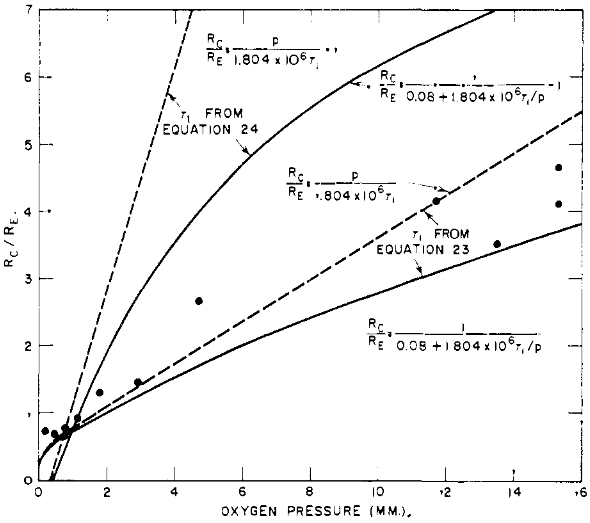

Fig. 6.—Relative rates of cleavage (R_C) and epoxidation (R_E) as a function of oxygen pressure in the oxidation of styrene at 50°.

We shall now consider the relation between rates of cleavage and epoxidation (R_C/R_E) and oxygen pressure in Fig. 6. This figure plots the experimental values of R_C/R_E as a function of oxygen pressure and shows that these values lie between the calculated limits. The calculated upper limit for R_C/R_E assumes that one ether link appears in the polyperoxide for each molecule of epoxide formed. The number of $-O_2M-$ units per chain irregularity is $k_{po}[M\cdot][O_2]/(k_p\cdot[M\cdot][M[+ k_{tr}[M\cdot][O_2])$.[40] The first term in the denominator is the rate at which $-MM-$ links are introduced. Complete depolymerization to an $MMO\cdot$ group following formation of a molecule of epoxide decreases the number of units in that irregularity, but not the frequency with which some irregularity appears. The second term in the denominator represents the rate at which the polyperoxide molecule is interrupted by chain transfer. From the mechanism for this reaction in section 5 and the relative rates of this reaction and a propagation reaction at 1–4 atmospheres,[4] $k_{tr}[M\cdot]\cdot[O_2]$ will be set equal to 0.04 $k_{po}[M\cdot][O_2]$. With this mechanism, R_C/R_E will be one less than the average number of uninterrupted $-O_2M-$ units in a monomer radical which rearranges to epoxide

$$\frac{R_C}{R_E} = \frac{k_{po}[M\cdot][O_2]}{2k_p[M\cdot][M] + 0.08\, k_{po}[M\cdot][O_2]} - 1 = \frac{1}{0.08 + 1.804 \times 10^6 r_1/p} - 1 \tag{36}$$

The effective value of r_1 for this equation is given by equation 24. The calculated lower limit for R_C/R_E assumes that all the terminal $MMO\cdot$ radicals decompose to $MCH_2\cdot$ and benzaldehyde, and that the resulting $MCH_2\cdot$ radical behaves like an $M\cdot$ radical in further propagation. The -1 term in equation 36 is therefore omitted. The effective value of r_1 for this equation is given by equation 23. Then

$$\frac{R_C}{R_E} = \frac{1}{0.08 + 1.804 \times 10^6 r_1/p} \tag{37}$$

The solid lines in Fig. 6 evaluate R_C/R_E by equations 36 and 37.[41] At oxygen pressures above 1 mm., the experimental values for R_C/R_O clearly rise with the oxygen pressure as required by the mechanism in Table III. These values also lie between the limits set by equations 36 and 37. At lower pressures, these equations are inapplicable, either because repeated depolymerization to the same irregularity requires a modified treatment, as with α-methylstyrene in section 8.4, or because of the side reaction described below. The broken lines in Fig. 6 correspond to equations 36 and 37 with the chain transfer term (0.08) omitted. This term clearly contributes a large proportion of the total irregularities as the pressure increases.

Another possible explanation for the high value of R_C/R_E below 1 mm. pressure is that some excess cleavage may arise by reaction 38

$$M\cdot + MO_2\cdot \xrightarrow{k'_{tom}} 2MO\cdot \tag{38}$$

Reaction 38 can be rationalized as follows. Combination of two unlike radicals liberates about 80 kcal./mole, while only half this energy is required to rupture the adjacent O–O bond, with the production of two alkoxy radicals.[42] The alkoxy radicals thus produced then decompose by reactions 9 or 9a. Such a reaction would permit immediate cleavage without preliminary formation of epoxide and thus increase R_C/R_E over calculated values in Fig. 6.

Considerations above have strongly supported reactions 8 and 9 for epoxidation and cleavage below 20 mm. pressure of oxygen. At 26 and 75 mm. pressure of oxygen, the rate of epoxidation was low and subject to large experimental error. At higher pressures, no epoxide at all was found by

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[38] Without the correction factor, R_M/R_O, the indicated value of $k_e/9.35 \times 10^{-4}$ is still lower at low pressures, little changed at high pressures.

[39] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

[40] This relation fails when three or more M units appear between two O_2 units. However, since oxygen has much more tendency to enter the copolymer after $\sim\!\sim O_2MM\cdot$ than after $\sim\!\sim O_2M\cdot$ (section 4.5), the error is probably negligible when $R_M/R_O < 2$. Only in expt. 107 in Table V is this requirement not met, and this experiment seems unreliable anyway.

[41] Since the coefficient 1.804×10^{-6} contains a factor, [M] = 8.43 mole/l., these equations apply at 50° only in the absence of solvents.

[42] The absence of an effect of [ABN] detracts from this suggestion, but R_C may be limited by oxygen uptake more than by radical interaction. The formation of two alkoxy radicals in this manner has previously been postulated by F. H. Seubold, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **73**, 18 (1951), for other oxidations at high temperatures. See also E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, *Disc. Faraday Soc.*, **10**, 242 (1951). A. B. Callear and J. C. Robb, *Trans. Faraday Soc.*, **51**, 649 (1955), have proposed for the hydrogen–oxygen reaction at low oxygen pressures that $H\cdot + HO_2\cdot \rightarrow 2HO\cdot$. Such non-terminating reactions of two radicals may account for the unexpectedly low φ values (<7) observed in many autoxidations.[11]

the infrared method used. Figure 7 shows the relation between cleavage and oxygen pressure above 20 mm. By considering R_C/R_O instead of R_C alone, the agreement among experiments is improved. The curve in Fig. 7 corresponds to

$$\frac{R_C}{R_O} = \frac{15}{p} + 0.03 \qquad (39)$$

This relation states that 3% of the oxygen reacting appears as cleavage products at all pressures, in a pressure-independent reaction, and that additional cleavage occurs as the pressure is reduced. This pressure-dependent cleavage apparently comes from depolymerization 9, following epoxidation 8, even when epoxidation was not detected. Equation 40 indicates the expected relations at pressures high enough so that the only important irregularities in the polyperoxide are the chain ends and so that equation 39 applies. Here, R_C refers only to pressure-dependent cleavage.

$$\frac{R_C}{R_O} = \frac{15}{p} = \frac{k_e[\mathrm{M}\cdot]R_C/R_E}{k_{po}[\mathrm{M}\cdot][\mathrm{O}_2]} = \frac{k_eR_C/R_E}{9.35 \times 10^{-6}pk_{po}} \qquad (40)$$

From equation 32 and the average of k_e/k_{po} in four experiments at 11–16 mm. pressure,[43] 1.93×10^{-5}, we calculate that $R_C/R_E = 7.3$ at 1 atm. of oxygen. From molecular weights of polyperoxides,[4] and also from equations 36 and 37, R_C/R_E should be 11-12 at 1 atm., and we can calculate that k_e/k_{po} should be 1.3×10^{-6} at the same pressure. Considering the errors in measuring R_E at 11–15 mm., the errors in determining the molecular weight of styrene peroxide made at 1 atm. pressure, and the possibilities of changes in k_e, k_{po} and particularly in k_{tr} in oxidations at 15–750 mm., the calculations above support the conclusions that pressure-dependent cleavage at high pressures as well as at low pressures arises mostly by depolymerization reaction 9, and that depolymerization is usually complete.

5. Summary and Conclusions

The data and conclusions in the previous sections will now be reorganized to give a concrete picture of what goes on in the oxidation of undiluted styrene (8.43 M) in the presence of 0.01 M ABN at 50°. The data are summarized in Fig. 1. In the absence of oxygen (k_p = 123 l./mole/sec.),[39] styrene radicals grow (reaction 2) at the rate of a thousand steps per second per radical and their concentration is about 10^{-7} M. At one atmosphere of oxygen, oxygen is around 10^6 times as reactive as styrene on a molar basis (section 4.5), but its concentration is only 0.0071 M. Therefore, the chance that a styrene radical will react with oxygen (reaction 3) is 900 times the chance of reaction with styrene. The resulting peroxide radical always reacts with styrene (reaction 4), producing mostly a polyperoxide, and the calculated monomer–oxygen ratio in the products is 1.001, indistinguishable experimentally from unity. Under such conditions, a styrene radical lasts only about 10^{-6} second before it reacts with oxygen. Nevertheless, about 0.3% of these styrene radicals rearrange to styrene oxide and alkoxy radicals (reaction 8), before they react with an oxygen molecule, and each of these alkoxy radicals depolymerizes rapidly to give 1–50 molecules each of benzaldehyde and formaldehyde (reaction 9) before either the solvent styrene or oxygen can interfere (section 4.6). The easy reaction of styrene radicals with oxygen produces peroxide radicals. These react relatively slowly with styrene, are by far the most plentiful radicals in solution, and are almost entirely responsible for termination of kinetic chains (reaction 7). Nevertheless, the formation of cleavage products, in a pressure-dependent reaction, shows that styrene radicals do have a significant life even at one atmosphere. These styrene radicals must also account for part of the slow change in over-all rate with pressure in the same region (reaction 6, section 4.1). At one atmosphere of oxygen, and above, a small proportion of the styrene and oxygen are converted directly to aldehydes, in a reaction independent of oxygen pressure (reaction 11 or 12, section 4.6).

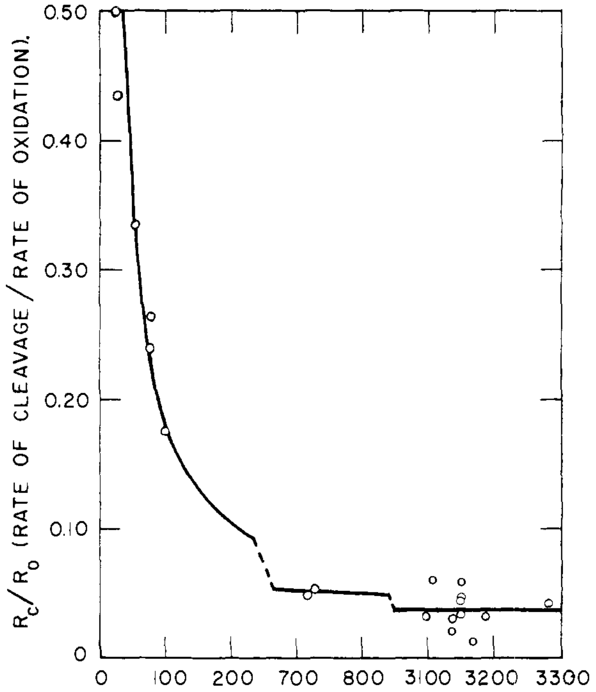
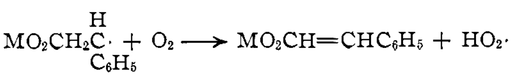
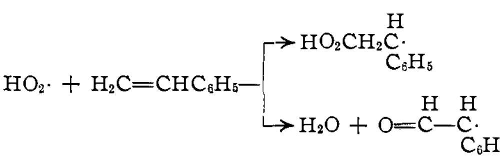


Fig. 7.—Relative rates of cleavage (R_C) and total oxidation (R_O) of styrene at 50° as a function of oxygen pressure. Experimental points from Fig. 1 in paper I[4] at 25, 50, 100 and 730 mm. are included.

Since about 560 molecules of styrene and oxygen react per ABN molecule decomposed, and since the polyperoxide averages $(C_8H_8O_2)_n$ where n is 22–30, the molecular chains must end by some chain transfer mechanism. Our knowledge of the end groups is insufficient to establish the mechanism,[4] but the following net reactions seem most plausible



$$\mathrm{MO_2CH_2}\underset{\mathrm{C_6H_5}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot + \mathrm{O_2} \longrightarrow \mathrm{MO_2CH{=}CHC_6H_5} + \mathrm{HO_2}\cdot \qquad (41)$$



$$\mathrm{HO_2}\cdot + \mathrm{H_2C{=}CHC_6H_5} \longrightarrow \mathrm{HO_2CH_2}\underset{\mathrm{C_6H_5}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot \qquad (42)$$

$$\mathrm{HO_2}\cdot + \mathrm{H_2C{=}CHC_6H_5} \longrightarrow \mathrm{H_2O} + \mathrm{O{=}}\overset{\mathrm{H}}{\mathrm{C}}\mathrm{{-}}\underset{\mathrm{C_6H_5}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot \qquad (43)$$

As the oxygen pressure is reduced, the styrene radicals have a longer life, and a greater chance of either reacting with styrene or of rearranging and depolymerizing. These reactions replace more

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[43] This method of evaluating k_e/k_{po} makes use of the identical initial slopes for all the sets of points in Fig. 5 and is therefore independent of the value chosen for r_1. This method postulates that k_e/k_{po} is constant in experiments at pressures above 15 mm. The postulate follows from the observations that there is little change either in chain composition (R_M/R_O), or in r_1 (equations 23–25), above this pressure.

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.

MENLO PARK, CALIFORNIA

[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,*]

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

RECEIVED SEPTEMBER 5, 1957

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.