[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Oxidation of Unsaturated Compounds. I. The Oxidation of Styrene[1]

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The rates and products of oxidation of styrene have been studied in the presence and absence of α,α'-azodiisobutyronitrile (ADBN) at 0.1 to 4 atmospheres of oxygen and at 35–85°. In the presence of initiator, the over-all rate of absorption of oxygen is proportional to $[\text{ADBN}]^{1/2}[C_8H_8]$. In the absence of initiator, the rate is proportional to $[C_8H_8]^{1.4}[O_2]^{0.4}$. Oxygen therefore participates in the initiation of thermal oxidation, and the rate of this initiation at 50° is 38 times the rate of initiation of thermal polymerization in the absence of oxygen. The products of oxidation are polymeric peroxide, benzaldehyde and formaldehyde. The two aldehydes are formed in equivalent quantities and are primary oxidation products. The ratio of polyperoxide to aldehyde formed at 50° varies from about 17 at 760 mm. to about 1 at 25 mm., and decreases with increasing temperature. The average composition of the polyperoxide formed at 50° varies from $(C_8H_8)_{1.5}O_2$ at 10 mm. pressure of oxygen to a limit of $C_8H_8O_2$ at high pressure. The peroxide formed at 1 atmosphere and 50° closely approximates this limit and has a number-average molecular weight of 3,000–4,000. The molecular weight is controlled by an unknown chain transfer mechanism. The peroxide is a poor initiator of oxidation and polymerization. The direct formation of aldehydes is the result of some reaction of a polyperoxide radical ending in a styrene unit, probably a unimolecular reaction of this radical. An 18% conversion to polyperoxide was obtained by stirring a 0.02 *M* solution of ADBN in styrene at 50° for 24 hours under an atmosphere of oxygen and precipitating the polymer with methanol.

The object of the work to be described in this series of papers was to study the oxidation of unsaturated compounds with reactive double bonds and to investigate the reactions of some of the polymeric peroxides obtained. Most of the previous work on the oxidation of unsaturated compounds[2] has been concerned with unsaturated hydrocarbons containing double bonds which are relatively unreactive in copolymerization.[2a] Such unsaturated compounds have reacted with peroxide radicals in chain oxidation reactions to give substituted allyl radicals and then the corresponding allyl hydroperoxides. Much less attention has been given to unsaturated compounds with reactive double bonds. Here, two kinds of reactions have been recorded, copolymerization with oxygen to form a polyperoxide and cleavage of the unsaturated compound at the double bond to give carbonyl compounds, but both reactions have seldom been reported with the same unsaturated compound. The present paper will show that the autoxidation of styrene by a free radical mechanism gives two simultaneous reactions, a copolymerization of styrene with oxygen, and a direct cleavage of styrene to benzaldehyde and formaldehyde. The two processes involve a common intermediate, a free radical ending in a styrene unit, and both the composition of the copolymer and the fraction of reacting styrene converted to aldehydes depend on the oxygen pressure. We shall consider first the rates and then the products, of the styrene–oxygen reaction at 50–80°, mostly at pressures above 100 mm. Next, we shall take up the question of end groups in the polymer and the mechanism by which the molecular weight is regulated. Finally, some aspects of the mechanism of thermal initiation and aldehyde formation will be considered. The second paper[3a] will consider the reactions of styrene peroxide. The third[3b] and fourth[3c] papers will consider the autoxidation of indene. Subsequent papers will present some novel phenomena observed in oxidations at oxygen pressures below about 100 mm. and will also consider the oxidation of some other unsaturated compounds. There, the reported effects of oxygen on polymerization[4] will be re-evaluated, since the rate of reaction of styrene passes through a minimum near 1 mm. pressure of oxygen.[5]

The styrene–oxygen copolymer, $(\text{–CH}_2\text{CH(C}_6\text{H}_5)\text{–O}_2\text{–})_n$, of molecular weight about 5,000 has been prepared previously by polymerization of styrene in the presence of oxygen, first, in emulsion by Bovey and Kolthoff,[6] subsequently in bulk by Barnes, Elofson and Jones.[7] This peroxide is less easily precipitated by non-solvents than is polystyrene, and it responds poorly to conventional peroxide tests. We conclude that some previous oxidations of styrene yielded polyperoxide which either was not found or was not identified as such.[5,8–10] We have no evidence that styrene can give any polymer except polyperoxide when the solution is saturated with oxygen near a pressure of one atmosphere.[11] However, some of the investigators who failed to report polyperoxide from styrene did report the formation of benzaldehyde and formaldehyde.[5,8,9] Medvedev and Zeitlin[9] reported that 90% of the oxygen absorbed at 70–90° appeared as aldehydes.

Experimental

Reagents.—Styrene (Dow N-99) was freed of inhibitor by washing with alkali and by fractional distillation. It was stored under nitrogen at about 10°. Prior to each experiment it was vacuum distilled. The free radical initiator, α,α'-azodiisobutyronitrile, hereafter designated ADBN, was obtained from commercial sources, recrystallized from

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[1] Presented before the Organic Division at the Chicago Meeting of the American Chemical Society, September 8, 1953.

[2] The field has been reviewed by J. L. Bolland, *Quart. Revs.* (*London*), **3**, 1 (1949), and L. Bateman, *ibid.*, **8**, 147 (1954).

[2a] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[3] (a) F. R. Mayo and A. A. Miller, THIS JOURNAL, **78**, 1023 (1956); (b) G. A. Russell, *ibid.*, 1035 (1956); (c) G. A. Russell, *ibid.*, 1041 (1956).

[4] F. A. Bovey and I. M. Kolthoff, *Chem. Revs.*, **42**, 491 (1948); C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 186.

[5] A minimum rate, without data, is also mentioned by H. Trenne, *Chem. Z.*, **74**, 692 (1950).

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

[7] C. E. Barnes, R. M. Elofson and G. D. Jones, *ibid.*, **72**, 210 (1950).

[8] N. A. Milas, *Proc. Natl. Acad. Sci.*, **14**, 844 (1928).

[9] S. Medvedev and P. Zeitlin, *Acta Physicochim. U.R.S.S.*, **20**, 3 (1945).

[10] H. Boardman and P. W. Selwood, THIS JOURNAL, **72**, 1372 (1950).

[11] G. A. Russell (ref. 3b) has arrived at a similar conclusion in the oxidation of indene.

petroleum ether and vacuum dried. The oxygen was 99.3–99.5% pure, the principal impurities being nitrogen and hydrogen.

Apparatus.—Oxygen absorption took place in shaker flasks in a constant-temperature bath. Rates were followed with a manometer and gas buret. For rate measurements at 4 atmospheres of oxygen, a calibrated Bourdon-type pressure gage was used in conjunction with a thick-walled reaction flask.

In the experiments at reduced oxygen pressures, where periodic analyses of products were made, rapidly stirred styrene was exposed to a continuous flow of oxygen which was diluted by the proper amount of nitrogen. The two gases were metered through calibrated capillary flowmeters and premixed before entering the reaction vessel. Loss of styrene vapor was kept at a minimum by a water-cooled reflux condenser.

Analyses.—The major products of the reaction of styrene and oxygen under the conditions of this work were polymeric styrene peroxide, benzaldehyde and formaldehyde.

Several iodometric methods were tried for the analysis of styrene peroxide. Although a completely satisfactory procedure could not be found, that described below was the best available.

The volatile monomer was separated from a 1- or 2-ml. sample of oxidized styrene by evacuation at room temperature. The residual polymeric peroxide was dissolved in 1 ml. of acetic anhydride and the solution was added dropwise to 1 ml. of constant-boiling hydriodic acid in a 100° bath over a period of 30 seconds. The reaction was allowed to continue for an additional 30 seconds and the resulting solution, containing liberated iodine, was diluted with water and titrated with 0.1 *N* sodium thiosulfate. In all operations CO_2 pellets were added to exclude air. After a small blank correction this method gave peroxide contents which agreed within 5% with the oxygen contents of known samples.

The constant-boiling hydriodic acid used should contain very little or no free iodine. The commercial reagent contains preservative hypophosphorous acid and some excess water, which were removed by two distillations. For the procedure given, the 1-minute total reaction time is critical; the percentage theoretical iodine found in known samples ranged from 95% in 0.5 minute (from the start of addition of peroxide) to 108% in 2 minutes and 210% in 2 hours. Benzaldehyde does not interfere with the determination, but styrene (ordinarily removed by evacuation), α-hydroxyacetophenone and phenylglycol do. The latter liberated iodine as fast, and in the same proportion, as peroxide. The method is therefore unsuitable for following the decomposition of peroxide.

Benzaldehyde was determined in samples of oxidized styrene by precipitation of the dinitrophenylhydrazone, using as reagent a solution of 3 g. of 2,4-dinitrophenylhydrazine (DNPH) in 100 ml. of methanol and 5 ml. of concd. hydrochloric acid. A 1- or 2-ml. sample of oxidized styrene solution was shaken with 10 ml. of methanol, and the precipitated or dispersed polymeric peroxide was separated by filtration. On addition of excess DNPH reagent to the filtrate, precipitation of the hydrazone occurred within a few minutes. After standing for at least an hour, the hydrazone was collected on a sintered glass funnel, dried at 100° and weighed. Melting points for the crude hydrazone obtained from the oxidized styrene were in the range 233–240°. Samples recrystallized from acetone and benzene melted at the recorded point for the 2,4-dinitrophenylhydrazone of benzaldehyde, 237°. A 1-ml. sample of styrene containing 10^{-4} mole of benzaldehyde gave 99% of the theoretical hydrazone by this gravimetric method. Methanol-soluble styrene peroxide of low molecular weight did not interfere. Measurements of the solubilities of the hydrazones of benzaldehyde and formaldehyde in methanol showed that the latter was about 300 times more soluble at room temperature. Thus, the presence of a small proportion of formaldehyde did not interfere with the benzaldehyde determination. Further, most of the monomeric formaldehyde formed in the styrene oxidation was removed by partial evacuation of the liquid sample prior to the benzaldehyde determination.

In a few experiments, quantitative measurements of the formaldehyde formed in the oxidation were made by precipitation and weighing of the dimethone derivative. Such measurements showed that formaldehyde and benzaldehyde are formed in approximately equivalent amounts.

Larger-scale Experiments.—Several experiments were carried out by stirring mixtures of 878 g. (1 liter at 50°) of styrene and 3.28 g. ADBN (0.02 mole) for 24 hours at 50° in slow streams of oxygen at 1 atmosphere pressure. Some of these are described below to indicate (1) the best material balance obtained, (2) a simple preparation of styrene peroxide, (3) the change in over-all rate with time, (4) the constant ratio of peroxide and aldehyde formation, and (5) rates for comparison with those to be presented later.

In the following experiment, 96.4% of the initial styrene and 100.7% of the weighed oxygen uptake are accounted for. 17.7% of the initial styrene was converted to 100% peroxide, 1.5% to aldehydes and 0.03% to α-hydroxyacetophenone. After allowing for decomposition of 0.74 g. of ADBN, 97.5% of this initiator is accounted for. In this experiment, the unabsorbed gas was passed through water at 0° and a trap at −78°. After 24.0 hours, the reaction mixture was cooled to 5° in a stream of oxygen while small portions were successively concentrated up to a liquid temperature of 30° below 1 mm. pressure. The distillate thus obtained 10.2 g. of benzaldehyde (by infrared absorption) and 558.4 g. of styrene (by difference). No unknown absorption band was found. The polyperoxide in the distillation residue was precipitated with methanol and was washed with this solvent until it became stiff. The polymer was dissolved in benzene and precipitated and washed with methanol, then redissolved and reprecipitated. This last polymer was then dissolved in benzene and concentrated at reduced pressure to remove methanol, and this solution and concentration were repeated once more. A small aliquot of the resulting solution was evaporated in a film for 15 minutes at 50° and 0.5 mm. pressure. It was found to contain 83.0% non-volatile material which analyzed for 71.6% C and 5.5% H, corresponding to 205.0 g. of 95.3% peroxide. From these figures, the whole benzene solution of the peroxide contained 195.3 g. of 100% peroxide and 9.7 g. of other "non-volatile material." This latter material included about 0.2 g. of polystyrene formed during concentration (as indicated by recoveries from some complete peroxide decompositions) and an estimated 0.8 g. of excess styrene in the polyperoxide (*cf.* Table IV), but was mostly benzene not removed from the polymer under the conditions employed.

The methanol and benzene washings were concentrated at reduced pressure up to a liquid temperature of 20° at 50 mm. The distillate contained 83.4 g. of styrene by bromine titration. The residue was further concentrated up to a liquid temperature of 30° at 0.4 mm., yielding 2.1 g. of benzaldehyde (DNPH method) and 25.9 g. of styrene (by difference). The distillation residue was resolved into 2.00 g. of recovered ADBN (from ether at low temperature), 7.64 g. more of methanol-insoluble polymer and 5.09 g. of methanol-soluble material not volatile at 40° and 0.3 mm. The insoluble polymer contained 77.2% carbon and is considered to consist of 5.29 g. of 100% peroxide and 2.35 g. of polystyrene formed during precipitation and concentrations. By infrared analysis, the soluble material contained 0.10 g. of benzene, 1.17 g. of benzaldehyde, 0.36 g. of α-hydroxyacetophenone, 0.46 g. of ADBN (by $C{\equiv}N$ absorption) and 3.00 g. of low-molecular weight styrene peroxide (by difference). That the remaining material is essentially styrene peroxide is supported by carbon analyses on other methanol-soluble polymers and their decomposition into benzaldehyde and formaldehyde on heating.

In the two traps (through which gas was exhausted) were found 5.68 g. of styrene and 0.46 g. of formaldehyde (as dimethone derivative). An additional 1.57 g. of insoluble paraformaldehyde was found in the reaction vessel. When corrections are made for products in the traps and for 0.13 g. of nitrogen calculated to have been lost by decomposition of 22.6% of the ADBN in 24 hours,[12] the oxygen absorbed, by weight gain of the reaction vessel, was 49.7 g. Only 0.068 mole of formaldehyde was found as compared with 0.128 mole of benzaldehyde. Since the ratio of formaldehyde to benzaldehyde was variable but attained a value somewhat greater than unity in another experiment, the balance assumes that these aldehydes are formed in equal quantities, the missing formaldehyde being dissolved as monomer or suspended as polymer in the reaction mixture.

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

For a convenient preparation of methanol-insoluble peroxide, mixtures like that above were simply poured into 2 liters of cold methanol after 24 hours reaction at 50°. The product was washed and reprecipitated as described above, and the methanol-soluble material was rejected. Conversions were 19.4 and 17.8% (expt. 38) of 100% peroxide, slightly better than the 17.0% obtained at this stage in the material balance experiment.

The rate of oxygen absorption was followed in one experiment like the material balance experiment. Oxygen was passed through a wet test meter, dried by cooling to −78°, passed into the reaction mixture and exhausted through a second wet test meter. The oxygen uptake was 51.0 g. by weight change of the reaction mixture, 51.6 g. by the meters (41% of that available) and 53.4 g. by the oxidation products found. The latter value corresponds to 19.8% oxidation of the initial styrene. Of the oxygen reacting, 93.5% appeared in the peroxide first precipitated by methanol, 1.9% in other peroxides and 4.6% as aldehydes, in the same range as the other experiments. The over-all rate of oxygen absorption by the meters was 0.0672 mole/l./hr. of styrene, but the rate decreased smoothly from 0.0954 mole/hr. during the first hour to 0.0688 mole/hr. during the eighth hour and to 0.0586 during the last three hours. A smaller decrease was observed in expt. 38, to be described next. Experiment 38, to which repeated reference is made, shows that the ratio of peroxide to benzaldehyde formed remains constant with time within experimental error. One-ml. aliquots were withdrawn periodically and infrared absorption bands were measured to determine peroxide (7.35 μ) and benzaldehyde (12.07 μ). Final determinations corresponded to 17.8% conversion of styrene to methanol-insoluble peroxide and 1.2% conversion to benzaldehyde. The fractions of the ultimate increases in absorption for peroxide and benzaldehyde, respectively, at various times were: 1.55 hr., 7.6%, 3–11%; 3.2 hr., 15%, 14%; 7.5 hr., 34%, 32%; 24 hr., 100%, 100%. In the oxygen meter experiment, 36.6% of the ultimate oxygen was absorbed in 7.5 hr., when 31.2% of the time had elapsed.

The above yields for 24-hr. experiments are summarized here for comparison with rates in smaller and shorter experiments to be discussed later. About 18.5% of the styrene is converted to peroxide and about 97% of this is easily precipitated by methanol. The rate of aldehyde formation is 6% of the rate of peroxide formation, and the yields of benzaldehyde average 1.2% in 24 hours. The initial rates for 0.01 *M* ADBN should be 0.83–1.00 times the 24-hr. average with 0.02 *M* initiator used above, depending on which ratio of initial-to-average rate is chosen.

Results and Discussion

Rates of Oxygen Absorption by Styrene at 50°.—The effects of monomer and initiator concentrations on the rate of absorption of oxygen at one atmosphere are shown in Table I. Rates were measured to only about 5% conversion and were constant in this range. The data show that the rate of oxygen absorption is proportional to the first power of the styrene concentration and to the square root of the initiator concentration. Similar measurements at oxygen pressures of 3120 mm. (4.1 atm.), 760 mm., 200 mm. and 100 mm. showed that the rate of oxygen absorption changed only slightly with oxygen pressure over this range but began to decrease at lower pressures.

TABLE I

RATES OF OXYGEN ABSORPTION BY STYRENE AT 50° AND 1 ATMOSPHERE

[Styrene], mole/l.	[ADBN],[a] mole/l.	Rate, mole/l./hr.	$\frac{\text{Rate}}{[\text{Styrene}][\text{ADBN}]^{1/2}}$
8.45	0.100	0.19	0.0070
	.010	.056	.0066
	.001	.016	.0059
4.22[b]	.01	.028	.0066
1.69[b]	.01	.010	.0060

[a] ADBN = α,α′-azodiisobutyronitrile. [b] Bromobenzene used as diluent.

Table II shows the effect of oxygen pressure on the rate of absorption of oxygen by styrene in the absence of added initiator. For increased sensitivity, a dibutyl phthalate manometer was used to measure pressures in this table. The data indicate a rate proportional to $[C_8H_8]^{1.38}[O_2]^{0.37}$. Comparison with the relation in the presence of ADBN suggests that the initiation step is first order in both styrene and oxygen.

TABLE II

RATES OF THERMAL OXIDATION OF STYRENE AT 50°

[Styrene], moles/l.	P_{O_2}, mm.	Rate, mole/l./hr.	$\frac{\text{Rate} \times 10^4}{[C_8H_8]^{1.38}[P_{O_2}]^{0.37}}$
8.45	727–735	0.00347	0.15
	288–290	.00225	.14
	90–97	.00160	.15
4.22[a]	730	.00143	.16
2.11[a]	730	.00051	.15

[a] Chlorobenzene used as diluent.

Effect of Temperature on Rate of Oxidation of Styrene.—The effect of temperature on the rate of absorption of oxygen by styrene is summarized in Table III. Since the thermal rate is pressure-dependent, the "*k*" values for such experiments assume that the effective oxygen concentration in solution depends on oxygen pressure but not on temperature. The data in Table III lead to over-all activation energies of 25.4 and 23.0 kcal./mole, respectively, for the initiated and thermal oxidations.

TABLE III

EFFECT OF TEMPERATURE ON RATE OF OXIDATION OF STYRENE

Temp., °C.	$[C_8H_8]$,[a] moles/hr.	P_{O_2},[b] mm.	Rate, mole/l./hr.	*k*[c]
35	8.58	749	0.0098	1.13[d]
50	8.45	735	.060	7.4[d]
65	8.30	610	.365	44.0[d]
50	8.45	735	.0034	1.5[e]
65	8.30	710	.0145	6.6[e]
80	8.20	670	.066	31.0[e]

[a] Concentrations of styrene are calculated from densities at the indicated temperature, as given by W. Patnode and W. Scheiber, THIS JOURNAL, 61, 3449 (1939). [b] Total pressure minus vapor pressure of styrene. [c] $k = 10^3$ rate/$[C_8H_8]$ for ADBN runs; $k = 10^5$ rate/$[C_8H_8]^{1.37}P_{O_2}^{0.38}$ for thermal runs. [d] $[\text{ADBN}]_0 = 0.010$ *M*. [e] No initiator added.

Initiation by Styrene Peroxide.—In order to test the effectiveness of styrene peroxide as an initiator, measurements of oxygen absorption by styrene were made with added polyperoxide. The peroxide used in these experiments analyzed as $[(C_8H_8)_{1.13}O_2]_n$ by combustion analysis and for 90% peroxide by the acetic anhydride–hydriodic acid method. Rates of oxygen absorption at 1 atmosphere were constant up to at least 5% conversion of styrene. Table IV shows that at 50° the rate in the presence of 0.1 *M* styrene peroxide is only 1.7 times the thermal rate (Table II). A similar concentration of ADBN (Table I) produces a rate which is 55 times the thermal rate. The rate of initiation by ADBN at 50° is calculated to be 1600 times the rate of initiation by the same concentration of peroxide units in styrene peroxide.[13,14] At 80°, the contributions of 0.046 and 0.2 *M* styrene peroxide are also comparable to the thermal rate in Table III.

TABLE IV

POLYPEROXIDE-INITIATED OXIDATION OF STYRENE

Temp., °C.	[Polyperoxide] g./l.	mole/l.[a]	Rate, m./l./hr.
50	13.6	0.10	0.0058
80	6.3	.046	.115
80	27.3	.20	.191

[a] On the basis of 100% polyperoxide with a molecular weight of 136 per peroxide unit.

Products of Oxidation of Styrene.—In order to determine the effect of oxygen pressure on the products of the oxidation of styrene, rapidly stirred styrene was exposed in a series of experiments to a continuous flow of oxygen diluted to a known concentration by nitrogen. At least five times as much oxygen was supplied as was consumed. Samples of the liquid product were analyzed periodically for peroxide and benzaldehyde by methods described earlier. When sufficient polymeric peroxide was prepared at a given oxygen pressure, the peroxide was isolated by concentration and precipitation with methanol,[15] dried and analyzed. Results are summarized in Table V. In the preparation of this table only the lowest carbon and highest oxygen contents from duplicate experiments are included. Erroneous high styrene contents may arise, either from lack of saturation of the reaction mixture by oxygen or from some polymerization of styrene during concentration of the reaction mixture *in vacuo*.

TABLE V

EFFECT OF OXYGEN PRESSURE ON THE COMPOSITION OF POLYPEROXIDE MADE AT 50°

P_{O_2}, mm.	Carbon, %	Hydrogen, %	Oxygen, %[a]	C_8H_8/O_2 in polymer	r_1[b] × 10^6
3120	71.0	5.71	23.5	1.0012[d]	
760[c]	70.3	7.0	..	1.005[d]	
	70.6	6.5			
50	71.4	6.20	..	1.06	3.3
25	73.1	5.87	21.2	1.15	4.1
10	76.5	6.90	17.3	1.48	5.2
5	77.0	6.30	16.4	1.56	3.1

[a] Oxygen by direct analysis. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.82; O, 23.51. [b] Ratio of rate constants for reactions of styrene radicals with styrene and oxygen, respectively. No allowance is made for styrene which is oxidized to aldehyde. [c] Expt. 38. [d] Calculated for $r_1 = 4 \times 10^{-6}$.

From the styrene–oxygen ratio in the polyperoxide, the relative reactivities of styrene and oxygen toward the styrene radical, r_1, can be calculated from the copolymerization equation,[2a] assuming that the peroxide radical cannot add to oxygen

$$\frac{d[C_8H_8]}{e[O_2]} = 1 + \frac{r_1[C_8H_8]}{[O_2]} \qquad (1)$$

The concentration of oxygen in styrene is assumed to be proportional to the oxygen pressure, and to be 0.007 mole/l. at 760 mm. pressure.[15a] The values of r_1 at low oxygen pressures are about 4×10^{-6}, indicating that at the same concentration oxygen would react 2–3 × 10^5 times as fast as styrene with the styrene radical. When this value of r_1 is used to calculate the compositions of peroxides formed at one and four atmospheres, the results are analytically indistinguishable from those for $C_8H_8O_2$.

From the above value of r_1 and the propagation constant in the polymerization of styrene at 50°, 123 l./mole/sec.,[16] the rate constant for the reaction of a styrene radical with molecular oxygen is 4×10^7 l./mole/sec. This very high value is close to that reported for another radical–oxygen reaction (7×10^7 l./mole/sec. for α-tetralyl with oxygen)[17] and also to those reported for interaction of two styrene radicals (about 1×10^7 l./mole/sec. at 50°).[16,18]

The effects of oxygen pressure on the rates of formation of polyperoxide and benzaldehyde at 50° with 0.01 *M* ADBN as initiator are shown in Fig. 1.[19] These data show that polyperoxide and benzaldehyde are formed concurrently from the beginning of the reaction at a ratio of rates which remains constant at each oxygen pressure. Only in the 25-mm. experiment does the formation of benzaldehyde show any possibility of an induction period, and the significance of this result is open to some question. The curves show clearly that the rate of formation of polyperoxide decreases and the rate of benzaldehyde formation increases as the oxygen pressure decreases. Although the rate of formation of peroxide is some 17 times the rate of formation of aldehyde at 760 mm. of oxygen, the rates are nearly equal at 25 mm. The rate data in Fig. 1, together with polymer compositions in Table V, show that the over-all rate of reaction of styrene decreases gradually from 0.057 mole/l./hr. at 760 mm. of oxygen to 0.048 mole/l./hr. at 25 mm. A later paper will show that the rate drops off further at lower pressures, then rises to about 0.10 mole/l./hr. in the absence of oxygen.

At constant oxygen pressure, the proportion of aldehydes formed increases with temperature. Figures 1 and 2 show that at 100 mm. pressure of oxygen the proportion of reacting oxygen converted to benzaldehyde is 0.18, 0.37 and 0.54 at 50°, 65° and 80°. The latter experiment employed no added initiator but gave concurrent formation of aldehyde and peroxide from the beginning of the reaction.

Medvedev and Zeitlin[9] studied the thermal oxidation of styrene at 70–90° to conversions of 3–5%. They reported concurrent oxidation to benzaldehyde and formaldehyde and polymerization to

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(13) (Rate of catalyzed initiation + rate of thermal initiation)/(rate of thermal initiation) = (catalyzed rate/thermal rate)^2 for each initiator.

(14) R. Inoue and M. Sumoto, *C. A.*, **47**, 345 (1953), by a similar method (details not available to us) have concluded that the rate of initiation by benzoyl peroxide is about 100 times the rate of initiation by styrene peroxide at 70–90°.

(15) About 3% of the lowest-molecular-weight peroxide is normally lost by this procedure.

(15a) Unpublished work by A. A. Miller.

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

(17) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*), **198A**, 252 (1949).

(18) G. M. Burnett and H. W. Melville, *Chem. Revs.*, **54**, 225 (1954).

(19) The rate of peroxide formation at 760 mm. oxygen agrees well with that indicated by the large-scale expt. 38. The aldehyde rate comes from that run. Although the data in the longest runs point to a gradual decrease in rate with time, as observed in large-scale runs, all the lines in Fig. 1 are drawn to represent average rate.

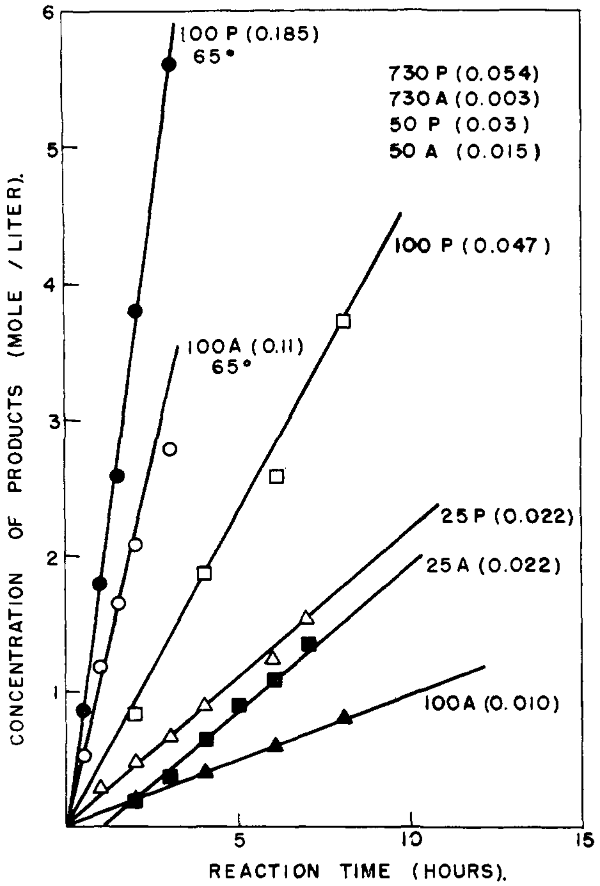

Fig. 1.—Rates of oxidation of styrene at 50° (except where 65° is indicated). The figures at the end of each line indicate the oxygen pressure in mm. of mercury, whether the data refer to polyperoxide (P) or aldehydes (A), and the average rate of oxygen consumption in mole/l./hr. in the indicated reaction. For clarity, results for 50 and 730 mm. are summarized.

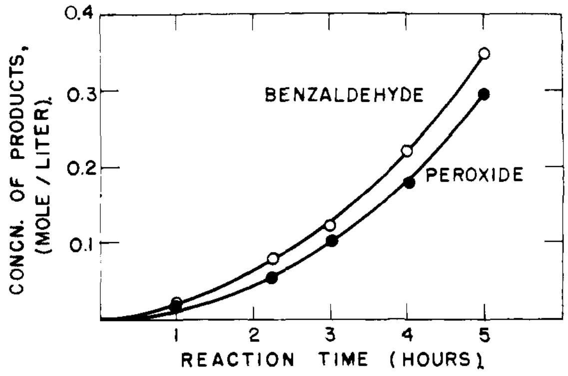

Fig. 2.—Thermal oxidation of styrene at 80° and 100-mm. pressure of oxygen.

polystyrene at a constant ratio of 2.5, this ratio being independent of mode of initiation, temperature or reaction time. In the present work, one of their oxidations at 80° (Table II of their paper) was duplicated and analyses for polyperoxide and benzaldehyde were made. The results are compared in Fig. 3. The combined rates of formation of peroxide and benzaldehyde found in the present work agree satisfactorily with the rate of oxygen absorption as measured by Medvedev and Zeitlin. In the present experiment, however, the polymeric product is *styrene polyperoxide*, as evidenced both by peroxide analysis and by combustion of the isolated polymer (71.0% C and 6.4% H, corresponding to $(C_8H_8)_{1.08}O_2$). Their erroneous conclusion about the composition of their polymer may be attributed to the failure of styrene polyperoxide to react in the mild peroxide test used by these authors and to their failure to analyze the polymer.

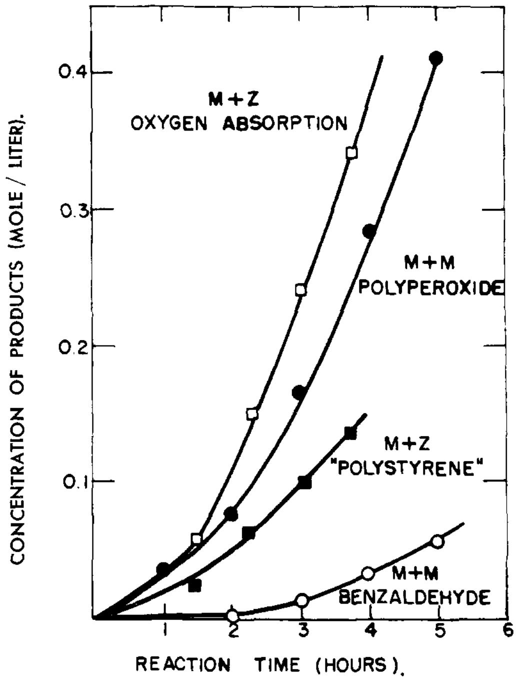

Fig. 3.—Thermal oxidation of styrene at 80° and 1 atmosphere of oxygen. Data of Medvedev and Zeitlin[8] (M. + Z.) are compared with our own (M. + M.).

Molecular Weight and End Groups of Styrene Peroxide.—This section will make the following points: (1) The normal copolymerization of styrene and oxygen at 50° gives a copolymer of number-average molecular weight 3000–4000. (2) The molecular weight is determined largely by some chain transfer mechanism. (3) Although hydroxyl and carbonyl end groups have been identified, not enough have been found to establish the transfer mechanism, and there is reason to suspect more than one.

In the large-scale expt. 38, where the polymer was isolated by immediate precipitation with methanol, the molecular weight was found to be 3300 ± 300 by freezing points of benzene solutions. Light-scattering measurements indicate that 3300 may be too low. The weight-average molecular weight on the same material in benzene was found to be 8000 ± 1000.[20] Since the molecular weight is determined by a transfer mechanism (see below), the number-average molecular weight should be 4000 ± 500, practically independent of the retention or loss of a little very low-molecular-weight polymer in precipitation. On the other hand, the known loss of 3% of such polymer of molecular weight about 350 results in revision of the cryoscopic molecular weight of all the peroxide to 2700. Numerous determinations of molecular weights by freezing points on other samples gave molecular weights mostly in

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(20) We are indebted to Mr. J. P. Bianchi for this determination.

the range 1500–2000, but since these polymers were subjected to more severe treatment in isolation, and since there is ample evidence that the polymer can be degraded but none that it can be condensed,[21] the highest value is preferred.

The mechanism which determines the molecular weight of styrene peroxide will now be considered. In expt. 38, cited above, 22.6% of the 0.02 M ADBN decomposed,[12] and 17.8% of the 8.43 M styrene was finally precipitated as polyperoxide of molecular weight 3300. Thus, each radical from the decomposing ADBN consumed 166 moles each of styrene and oxygen, and produced 7 moles of peroxide if the initiation was 100% efficient, more if it was less efficient.[22] It is difficult to escape the conclusion that the molecular weight is determined largely by some chain transfer reaction. Table VI shows that neither accumulating benzaldehyde nor the process which forms benzaldehyde can have more than a minor role in regulating molecular weight. A plot of $1/\overline{DP}$ for one-atmosphere runs against time extrapolates to $\overline{DP} = 23$ at zero time when no aldehyde is present. Similarly, a plot of $1/\overline{DP}$ at 7 hours against the reciprocal oxygen pressure extrapolates to $\overline{DP} = 30$ for infinite oxygen pressure, where aldehyde formation might be at a minimum and where the polymer should approach $(C_8H_8O_2)_n$ most closely. At neither limit does $\overline{DP}$ approach the estimated kinetic chain length, >166. Chain transfer of growing radicals with the polymer is also an inadequate explanation. If the transfer does not result in cleavage of the polymer, then transfer does not affect the number-average molecular weight. If transfer results in cleavage of already-formed polymer, then the molecular weight should drop rapidly with conversion and should approach the kinetic chain length at zero time, but it does not.

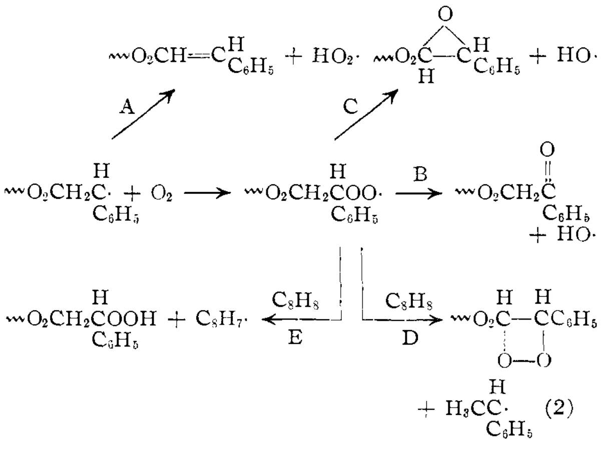
TABLE VI

EFFECT OF REACTION TIME AND OXYGEN PRESSURE ON MOLECULAR WEIGHT OF STYRENE PEROXIDE[a]

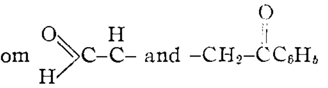
Oxygen press., atm.	1	1	4
Reaction time, hr.	1	7	7
Conversion to peroxide[b] (%)	93	95	99
Mole. wt. of peroxide[c]	3043	2724	3632
$\overline{DP}$ of peroxide[d]	22.4	20.0	26.7

[a] With 0.01 M ADBN at 50°. [b] From weight of polymer isolated by precipitation and measurement of oxygen absorbed. [c] Determined cryoscopically in benzene. [d] Degree of polymerization, average number of styrene or O_2 units per peroxide molecule.

The remainder of this section will show that the polyperoxide contains hydroxyl and carbonyl groups, but not enough to account for all the end groups or to establish the mechanism of chain transfer. Since the molecular weight is not very sensitive to oxygen pressure, the regulating step may be (1) an alternative to either propagation step, involving the same reactants, or (2) a unimolecular reaction of the peroxide radical. It cannot involve an unstable oxygen complex or hydrogen transfer between a styrene radical and styrene.[23] These limitations admit the following possibilities for regulation of the molecular weight.



Infrared, peroxide titration and molecular weight data are presented below. If these are accepted at face value, then a combination of mechanisms A and E is admissible, and mechanisms B, C and D are excluded, but the data are really inadequate to reach a decision. The ratio of the rate constants for the transfer step and the competing propagation step is $1/\overline{DP}$, about 0.04.

Infrared absorption spectra have indicated the presence of both hydroxyl and carbonyl groups. The most information comes from expt. 38, where 7.13 g. of polyperoxide (molecular weight, 3300) was fractionally precipitated three times from benzene with methanol. Infrared absorptions were compared for 10% solutions in carbon tetrachloride of the least soluble 1.28 g. and the most soluble 0.13 g. The lowest-molecular-weight (most soluble) material absorbed 4–5 times as strongly as the least soluble material at 2.80 μ, about twice as strongly at 5.75 and 5.90 μ. The absorbance at 2.80 μ in the most soluble fraction, due to hydroxyl, corresponded to one hydroxyl group (as in ethanol) in a molecular weight of 6400. The absorbances at 5.75 and 5.90 μ, which could arise from  $\mathrm{O{=}CH{-}\overset{H}{C}{-}}$ and $\mathrm{-CH_2{-}\overset{O}{\overset{\|}{C}}C_6H_5}$ groups, corresponded to one of each kind of carbonyl group (using α-phenylpropionaldehyde and acetophenone as standards) per 16000 molecular weight. Although this most soluble fraction was too small for a molecular-weight determination, its molecular weight may be taken as 1000 ± 500. Thus, about one-sixth of the polymer molecules seem to have one hydroxyl group and about one-eighth seem to have one carbonyl group, but the rest of the chain ends are unaccounted for. Unsaturated hydrocarbon, epoxide or cyclic peroxide groups would not be detected.

Several efforts were made to detect hydroperoxide end groups by the acetic anhydride–sodium iodide method of Nozaki.[24] This reagent attacks the dialkyl peroxide groups in styrene peroxide only slowly and incompletely. The best results were obtained with unfractionated peroxide 38. Determination of peroxide at intervals between 5 and 60 minutes, along with appropriate blanks, showed that the rate of liberation of iodine was constant in the interval from 20–60 minutes, and that extrapolation of this rate to zero time indicated the presence of one gram-mole of reactive peroxide per 6000 g. of polymer of average molecular weight 3300. If we assume that the reactive peroxide found by titration is hydroperoxide, then all (and more) of the hydroxyl found by infrared must be in hydroperoxide, little or none in alcohol groups. The hydroperoxide groups introduced by reactions A and E may partly decompose, with loss of water, to give the two kinds of carbonyl groups found in about equal quantities. There is nearly enough hydroperoxide by titration and total carbonyl by infrared to account for one end group for each molecule; the other end group would then be an undetected, unsaturated, hydrocarbon group. On the other hand, if the cyclic peroxide in D is rapidly attacked by the peroxide reagent, about 50% of the transfer may occur by mechanism D. The hydroxyl groups found by infrared may then arise by mechanisms B and C. In any event, the present data point to more than one transfer mechanism.

Mechanism of Oxidation of Styrene.—The data first presented show that the rate of the ADBN-initiated oxidation of styrene near one atmosphere pressure of oxygen is proportional to $[ADBN]^{1/2}[C_8H_8]$ and independent of oxygen pressure. The conventional mechanism of autoxidation of unsaturated hydrocarbons[2] needs only the substitution of an addition for a transfer step[6] to fit

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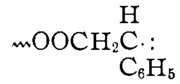
[21] Although thermal cleavage of peroxide may produce radicals which will grow to higher polymers in styrene and oxygen, rate studies in previous sections have shown that such reactions are unimportant.

[22] An efficiency of 60–70% is indicated by G. S. Hammond, J. N. Sen and E. C. Boozer, THIS JOURNAL, **77**, 3244 (1955).

[23] At least in the absence of oxygen, this reaction occurs only 1/17000 times as fast as propagation, which is much slower than the present reaction with oxygen; *cf.* F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

[24] K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

the present case, where M and M· represent styrene and the styrene radical,  $\sim\!\!\sim OOCH_2\overset{H}{\underset{C_6H_5}{C}}\cdot$:

$$\left.\begin{aligned} ADBN &\longrightarrow \\ M + O_2 &\longrightarrow \end{aligned}\right\}\begin{aligned} &\text{Indirectly 2 M}\cdot \quad (3) \\ &\text{or } 2MO_2\cdot \text{ radicals} \quad (3a) \end{aligned}$$

$$M\cdot + O_2 \longrightarrow MO_2\cdot \quad (4)$$

$$MO_2\cdot + M \longrightarrow M\cdot \quad (5)$$

$$2MO_2\cdot \longrightarrow \text{Non-radical products} \quad (6)$$

The kinetics are satisfied by reactions 3 and 4–6 in the presence of ADBN, by 3a and 4–6 in its absence. The rate of thermal initiation in styrene and oxygen may be related to the rate of thermal initiation in styrene alone by comparing both over-all rates of reaction with the over-all rates in the presence of 0.01 *M* ADBN. At one atmosphere of oxygen at 50°, the thermal rate is 0.062 of the rate at 0.01 *M* ADBN, from Tables I and II. In the absence of oxygen, the thermal rate at 50° (0.0011 mole/l./hr.)[25] is 0.010 the rate at 0.01 *M* ADBN (0.11 mole/l./hr.).[12,26] In spite of the low concentration of oxygen in styrene at a pressure of one atmosphere, the thermal initiation rate in the presence of oxygen is $(0.062/0.01)^2$ or 38 times the initiation rate in the absence of oxygen. In view of the complexities in thermal initiation in styrene[25] and the fractional order of the thermal oxidation reaction, the mechanism of thermal initiation is still obscure.

The most important contributions of this work are the discoveries that benzaldehyde and formaldehyde are formed concurrently with styrene peroxide and that the competition between these two reactions is determined by the oxygen pressure. The increase in yield of aldehydes as the oxygen pressure is reduced shows that aldehyde formation results from some reaction of growing chains which end in styrene radicals. Such an intermediate is the only one known to us which can increase in concentration as the oxygen pressure decreases. This intermediate is also responsible for polyperoxide formation and, therefore, for essentially all the absorption of oxygen. From the relative rates of formation of aldehydes and polyperoxide at 50–80°, the activation energy for aldehyde formation is only 6–10 kcal. higher than for reaction of styrene radicals with oxygen, already shown to require little or no activation energy. These considerations lead to the tentative conclusion that aldehydes result from a unimolecular reaction of the styrene radical

$$\sim\!\!\sim CH_2\overset{H}{\underset{C_6H_5}{C}}OOCH_2\overset{H}{\underset{C_6H_5}{C}}\cdot \longrightarrow \sim\!\!\sim CH_2\overset{H}{\underset{C_6H_5}{C}}\cdot + H_2C{=}O + BzH$$

This conclusion is consistent with the data in Fig. 1: the proportion of reacting oxygen which appears in aldehydes is nearly proportional to 1/(oxygen pressure) over a 30-fold change in pressure. Other possible mechanisms of aldehyde formation involving M· radicals seem to be excluded. Reaction with some other radicals would not be expected to require 6–10 kcal. more activation energy than is required for the addition of an oxygen molecule. Reaction with oxygen is excluded because less aldehydes are formed at high oxygen pressures. Reaction with styrene is not excluded by the available data but seems improbable.

Acknowledgment.—Several members of the Analytical Chemistry Unit, and also Mrs. D. K. Ladd and Miss G. Bess Rickman, have provided substantial assistance in some of the experimental work recorded in this and the succeeding paper. Dr. G. A. Russell has contributed to numerous discussions of the same work.

SCHENECTADY, NEW YORK

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[25] F. R. Mayo, THIS JOURNAL, **75**, 6133 (1953).

[26] The data of R. N. Haward and W. Simpson, *Trans. Faraday Soc.*, **47**, 212 (1951), interpolate to 0.094 mole/l./hr.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Oxidation of Unsaturated Compounds. II. Reactions of Styrene Peroxide[1]

BY F. R. MAYO AND A. A. MILLER

RECEIVED AUGUST 8, 1955

The reactions of polymeric styrene peroxide have been studied under the influence of heat, light, reducing agents, bases, acids and various other catalysts. High conversions to benzaldehyde and formaldehyde have been obtained by thermal decomposition with prompt removal of products, and to phenylethylene glycol by catalytic hydrogenation. Results of all decompositions are correlated by two mechanisms: (1) A free radical chain mechanism, initiated by initial cleavage of a peroxide link to alkoxy radicals, followed by alternate losses of benzaldehyde and formaldehyde, and (2) a series of disproportionations in which hydrogen atoms are transferred from carbon to the second oxygen atom of the adjacent peroxide link. The second scheme results in formation of α-hydroxyacetophenone and of equal parts of phenylglycol and phenylglyoxal. Since the aldehydes and hydroxy ketone are also affected by agents which decompose the peroxide, most decompositions have given complicated mixtures, and not all of the secondary products have been identified. Styrene peroxide can be estimated by its ability to oxidize mercaptans in the presence of bases.

Since polymeric peroxides made by copolymerization of oxygen and vinyl monomers[2] are potentially cheap materials which have received little attention, the object of the present work was to investigate the reactions of styrene peroxide. Emphasis was placed on finding clean reactions of possible synthetic value rather than on investigating complicated reactions. Because a large number of reactions have been tried, and because none has been investigated thoroughly, a general assessment of the field will be of more interest than details. Accordingly, we shall present first a summary of the

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[1] Presented at the Chicago Meeting of the American Chemical Society, Sept. 8, 1953.

[2] (a) A. A. Miller and F. R. Mayo, THIS JOURNAL, **78**, 1017 (1956); (b) A. A. Miller, F. R. Mayo and G. A. Russell, papers to be submitted to THIS JOURNAL.