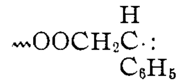
the present case, where M and M· represent styrene and the styrene radical,



$$\sim OOCH_2\overset{H}{\underset{C_6H_5}{C}}\cdot :$$

$$\text{ADBN} \longrightarrow \Big\{ \text{Indirectly } 2\ \text{M}\cdot \qquad (3)$$

$$\text{M} + O_2 \longrightarrow \Big\{ \text{or } 2\text{MO}_2\cdot \text{ radicals} \qquad (3a)$$

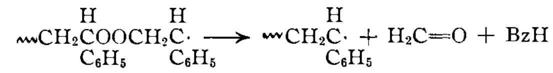
$$\text{M}\cdot + O_2 \longrightarrow \text{MO}_2\cdot \qquad (4)$$

$$\text{MO}_2\cdot + \text{M} \longrightarrow \text{M}\cdot \qquad (5)$$

$$2\text{MO}_2\cdot \longrightarrow \text{Non-radical products} \qquad (6)$$

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



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

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.

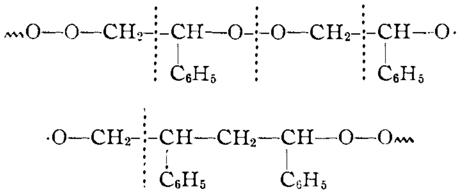
reactions of styrene peroxide, then the details of the present work. A subsequent paper[2b] will review the reactions of other polymeric peroxides.

Information on the reactions of styrene peroxide has been very scanty. Bovey and Kolthoff[3] reported that styrene peroxide exploded above 100°. Heating the peroxide in a sealed tube at 180° gave 60–80% yield of benzaldehyde, less formaldehyde, some gas, and (presumably) unidentified residues. Barnes, Elofson and Jones[4] attempted catalytic reduction of styrene peroxide with Adams platinum oxide catalyst, but could obtain only about 30% yield of phenylethylene glycol (phenylglycol). Electrolytic reduction of peroxide gave somewhat more glycol. Russell[5] obtained nearly quantitative yields of phenylglycol by reduction of the peroxide with lithium aluminum hydride. There can be no doubt that the structure of the peroxide is essentially $[-O-O-CH_2-CH(C_6H_5)-]_n$.

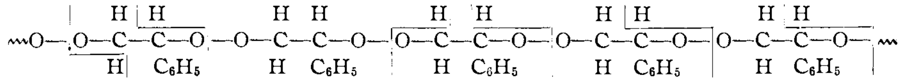
Summary and Conclusions.—Only two clean reactions of styrene peroxide have been found. Nearly quantitative yields of benzaldehyde and formaldehyde were obtained under several conditions. Good yields of phenylglycol were obtained by reduction, up to 70% with hydrogen sulfide or a mercaptan as reducing agent under weakly basic conditions, and as much as 80% with hydrogen and a Raney-type nickel catalyst.[5a] Most other conditions gave mixtures of products, often containing many components and unidentified compounds. In most cases, complications seemed to arise through secondary reactions of primary products. Study of the complications did not seem worthwhile either for practical applications or for fundamental knowledge of peroxide chemistry. In the following effort to present a consistent picture of these peroxide reactions, some conclusions are better founded than others, as may be judged from the supporting evidence under "Experimental Results."

The polymers used were nearly clear and colorless, brittle below 0°, and soft and sticky above 40°. They had molecular weights of 1500–3500, determined cryoscopically in benzene. The end groups were largely unidentified, but some carbonyl and hydroperoxide groups were present.[2a] All the polyperoxides were prepared at one atmosphere of oxygen and therefore averaged $[(C_8H_8)_{1.00-1.01}O_2]_n$.[2a] However, a little polystyrene accumulated during isolation.

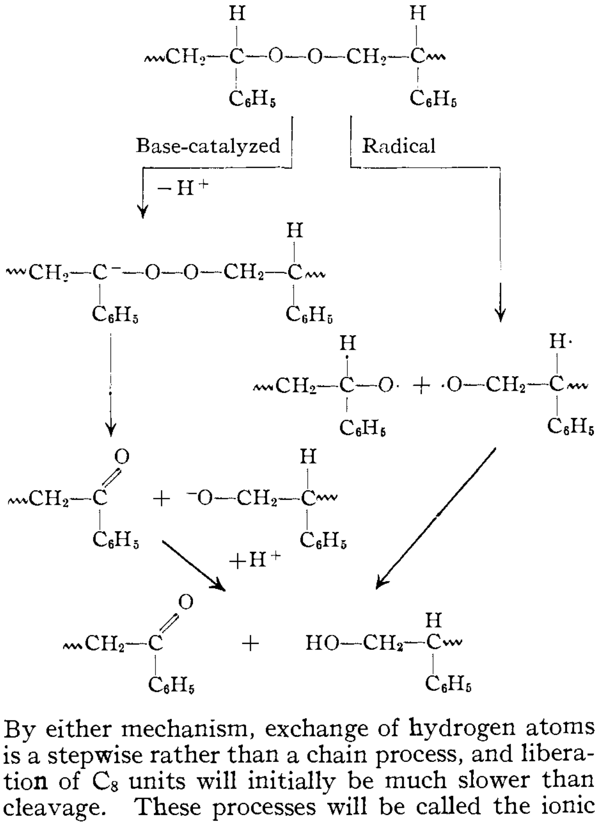
The principal reaction of styrene peroxide is cleavage of a peroxide bond into two alkoxy radicals, initiated by heat or light. These radicals then lose alternately benzaldehyde and formaldehyde units in an exothermic chain reaction which may be interrupted by a chain end, an extra styrene unit in the chain, another radical or some other reagent. This mechanism will be called the "chain mechanism." Usually chains are not long. Experiments on the photochemical chain reaction indicated a quantum yield of about 5 for a 0.5 *M* solution in benzene at 27°, lower at lower temperatures, higher at higher temperatures. The best retarders found are hydroquinone, styrene and α-methylstyrene.



The next most important reaction of styrene peroxides involves a rearrangement of hydrogen atoms among units in a peroxide chain. This reaction is particularly favored by basic catalysts[6] but occurs to various extents under most conditions.



If each styrene unit always loses one hydrogen atom and gains another, the sole product would be α-hydroxyacetophenone (unknown tautomer is mandelic aldehyde). If one unit gains two hydrogen atoms to become phenylglycol, then some other unit must lose two hydrogen atoms to become phenylglyoxal. The transfer may occur by a radical or non-radical mechanism. These illustrations do not necessarily represent the only products of disproportionation



By either mechanism, exchange of hydrogen atoms is a stepwise rather than a chain process, and liberation of C_8 units will initially be much slower than cleavage. These processes will be called the ionic

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

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

(5) G. A. Russell, *ibid.*, **75**, 5011 (1953).

(5a) This catalyst contained 0.7% chromium in the nickel; *cf.* N. V. Vengerova and E. A. Gasteva, *C.A.*, **32**, 1965 (1938); I. S. Scriabine, J. F. Billan, A. F. S. Bellone and M. Gaillard, U. S. Patent 2,502,348 (1950), *C.A.*, **44**, 4607 (1950).

(6) N. Kornblum and H. E. DeLaMare, THIS JOURNAL, **73**, 880 (1951), have reported such a reaction for α-phenethyl *t*-butyl peroxide

and radical *disproportionation mechanisms.* The disproportionation of two alkoxy radicals may well be a terminating step in the chain mechanism.

Under the influence of heat or light, styrene peroxide decomposes principally by the chain mechanism to give benzaldehyde and formaldehyde. In the absence of catalyst, the decomposition may become explosive above 100°. Often, only a portion of the sample explodes at one time, and when a small sample is placed in a flame, it sputters and gradually disappears in a series of puffs. The peroxide has not been exploded by striking or grinding, but one detonation occurred on heating a sample with phosphoric acid at 100° and reduced pressure. On storage in the dark at 7°, the peroxide keeps well; one sample stored as an 80% solution in benzene yielded only 0.6% benzaldehyde in 6.5 months.

In benzene solution or in the absence of a solvent, styrene peroxide decomposes to the extent of about 50% in an hour at 100° or in 10 hours at 80°. Starting with a 10% solution of peroxide in chloroform, 25% yield of benzaldehyde has been obtained in a 15-minute exposure to sunlight at 20°, and one-minute exposure at room temperature to a mercury lamp resulted in extensive decomposition and heating of the reaction mixture. In all cases, the benzaldehyde formed complicates the reaction. If the decomposition products are quickly removed from the decomposing peroxide, the reaction becomes much cleaner, and nearly quantitative yields of benzaldehyde and formaldehyde may be obtained. Decompositions of styrene peroxide in excess of benzaldehyde as solvent have given complicated mixtures like those ordinarily obtained when products are not removed.

The thermal and photodecompositions are always accompanied by some disproportionation products, principally hydroxyacetophenone. Phenylglycol frequently has been found. Phenylglyoxal has not been positively identified, although a clear yellow color frequently obtained in fractions boiling close to benzaldehyde strongly suggests its presence. The ratio of benzaldehyde to hydroxyacetophenone ranges from about 200 in the explosive decomposition at elevated temperatures and low pressures to about 3 in α-methylstyrene solution at 80° and about 2 in photodecompositions without solvent at room temperature. Apparently, radical decomposition chains are longest at high temperatures, shorter when retarded by solvents and least important at low temperatures. The importance of the disproportionation mechanism increases as that of the chain mechanism decreases, but whether disproportionation is a radical or non-radical process, or both, has not been established.

Base-catalyzed decompositions have been of particular interest because they proceed rapidly at room temperature by the disproportionation mechanism. However, their study has been discouraging because many of the primary products seem to be more sensitive to bases than the peroxide. Results may be accounted for in the following way. Primary products are α-hydroxyacetophenone, phenylglycol and phenylglyoxal. The first is cleaved to benzaldehyde and formaldehyde by bases. Base also causes disproportionation reactions of all the above products except phenylglycol: α-hydroxyacetophenone may be reduced to phenylglycol and oxidized to mandelic acid; phenylglyoxal may be reduced to hydroxyacetophenone, oxidized to phenylglyoxylic acid, or rearranged to mandelic acid; benzaldehyde yields benzyl alcohol and benzoic acid, and formaldehyde yields methanol and formic acid. In addition, base-catalyzed condensations lead to more complex unidentified products, and disproportionation of aldehyde mixtures leads to esters. The acids formed neutralize the bases, and in all cases continued slow addition of base is necessary to maintain decomposition of peroxide.

By serving as hydrogen donors, amines may cause a radical decomposition as well as a base-catalyzed reaction, for they are consumed in ways other than neutralization. About 50 mole % of piperidine was required to decompose styrene peroxide and evidence of N-hydroxypiperidine was found. Only 5 mole % of triethylamine, however, could effect nearly complete decomposition, and when acetic anhydride was used as solvent so that the hydroxyacetophenone would be protected by acetylation, the final yield of this disproportionation production was increased to 30%. *t*-Butylamine, a fairly strong base without α-hydrogen atoms, gave the slowest decomposition and the most hydroxyacetophenone, but the decomposition of peroxide was incomplete. Perhaps the amine was deactivated by condensation with accumulated carbonyl compounds. Ammonia may give similar results.

The interpretations above are based on identification of the following products of base-catalyzed decompositions: formaldehyde, formic acid, benzyl alcohol, benzaldehyde, benzoic acid, phenylglycol, α-hydroxyacetophenone, phenylglyoxal (by color and b.p. only), mandelic acid, phenylglyoxylic acid, methyl benzoate and methyl mandelate. The highest yields of individual products found in various experiments were: 49% benzaldehyde, 31% phenylglycol, 30% hydroxyacetophenone (as acetate), 29% paraformaldehyde, 26% benzyl alcohol, 14% benzoic acid and 5% mandelic acid (as acetate). Maximum yields of other identified products were below 5%.

Acids catalyze the decomposition of styrene peroxide to give benzaldehyde and formaldehyde as the principal identified products. Perchloric acid is most effective; sulfuric, toluenesulfonic and phosphoric are moderately effective, and acetic and benzoic have little effect; 0.5% of ferric stearate also gave a fast decomposition to aldehydes at 80°. These reactions tend to proceed either slowly or quickly, and intermediate rates have been hard to obtain. The products are mostly those of the radical chain mechanism. Although catalysis of a radical chain mechanism by acids is unexpected, the mechanism of the acid-catalyzed reaction has not been investigated.

Conventional catalytic reductions have been sluggish. Yields have been improved either by addition of an amine or by use of a large proportion (15% by weight) of a modified Raney-type nickel catalyst.[5a] Use of both amine and the modified catalyst has given 80% yields of phenylglycol.

Sulfhydryl compounds, particularly hydrogen sulfide, have been effective reducing agents, but a little base is also required. Yields of phenylglycol have ranged up to 70%. Catalytic quantities of aluminum isopropoxide failed to rearrange polyperoxide to esters, but an excess of the reagent gave 27% benzyl alcohol, 10% phenylglycol and 8% α-phenylglycerol as the only identified products. Evidently, disproportionation is a major reaction and benzaldehyde and formaldehyde result from the chain decomposition or from hydroxyacetophenone. Phenylglycerol must come from condensation of hydroxyacetophenone and formaldehyde,[7] followed by reduction. On the basis that two styrene peroxide units are required to give one phenylglycerol, the yield of the latter was 15%.

Experimental Methods

This section will present (1) our general procedure for investigating peroxide decomposition, (2) the isolation of styrene peroxide, (3) attempts to determine styrene peroxide and (4) some information on decomposition products. Our principal data on peroxide decompositions will appear in the last section, "Experimental Results." The polyperoxides used were prepared at one atmosphere pressure of oxygen by the procedures described previously for "larger scale runs."[2a] The polyperoxide is considered to be fairly uniform, and the variations in purity in Table I are thought to be due to polystyrene formed during isolation of peroxide and to benzene not readily removed by warming and evacuation.

General Procedure.—In decompositions 1–48, the products were identified mostly by isolating them or their derivatives. Benzaldehyde was determined as its 2,4-dinitrophenylhydrazone.[2a] The other compounds listed were usually isolated as solids, but because of their similar points and solubilities, separations and recoveries were poor. After expt. 48, benzaldehyde, hydroxyacetophenone, phenylglycol and most other products were usually determined by infrared analyses of fractions, made into 10 weight % solutions in chloroform. The separation procedure used varied with the circumstances, but the general approach to analyses will be indicated. All fractions and residues were weighed in an effort to account for all material or to determine how it was lost.

In decompositions at reduced pressures, distillates were collected in cooled traps. In other runs, the products were usually resolved roughly into recovered solvent, products containing one benzene ring (b.p. below 130° at 1 mm. pressure), higher boiling products (up to about 180° at 1 mm.), and less volatile or non-volatile products. If there was reason to think that considerable polymeric peroxide remained, products were concentrated by distillation up to a liquid temperature of 40–50° at 1 mm. The residue was then treated with excess methanol to precipitate polymer. This polymer was then extracted with methanol and dried for 15 min. at 50° below 1 mm. pressure. Such a product is listed as "recovered polymer" in Table I, and final distillation residues from methanol-soluble material are listed as "non-volatile material." If no polymer precipitation was carried out, the distillation residues include both non-volatile material and recovered polymer, and yield figures are given *between* those respective columns in Table I. The polymer precipitation, however, did not remove degraded peroxide which was soluble in methanol. The presence of such material was revealed by distillation of more benzaldehyde after collection of a benzaldehyde fraction, by evolution of formaldehyde gas, or a temperature rise in the material being distilled.

Most distillations were carried out in Claisen flasks with extended Vigreux-type necks. Solvents boiling below 100° were distilled at reduced pressure and discarded. Sometimes the benzene distillate was tested with dinitrophenylhydrazine reagent and found to contain a little benzaldehyde. Recovered acetic anhydride was redistilled to avoid loss of reaction products. Recovered styrene and α-methylstyrene were analyzed for benzaldehyde by infrared absorption and comparison with standards with these monomers as solvents. The principal identified products in most runs were benzaldehyde (b.p. about 90° at 30 mm.) and the hydroxyacetophenone–phenylglycol fraction (b.p. 85–120° at 0.5 to 1 mm.). These fractions were collected and analyzed, either separately or together, depending on their relative proportions. The still higher-boiling materials varied considerably in quantity and seemed to be mixtures containing complex benzoic esters, but little has been accomplished in resolving them. These products are listed as unidentified volatile and as non-volatile materials if a fraction was collected above 130° at 1 mm.; otherwise, the yield of all material not distilled below or with the phenylglycol fraction is indicated *between* the volatile and non-volatile columns.

Formaldehyde was not regularly determined. Occasionally it was determined as its methone derivative. Sometimes a deposit of paraformaldehyde was washed with benzene, dried and weighed. In most cases formaldehyde should be formed in quantities equivalent to benzaldehyde, and therefore only one of these aldehydes must be determined to account for the peroxide.

Isolation of Styrene Peroxide.—Styrene peroxide was usually prepared, stored and used as a 70–80% solution in benzene. In contrast to the pure peroxide, which was hard and brittle when cold, and sticky when warm, such a solution would flow slowly. These solutions were assayed by diluting a 0.2 to 0.3-g. sample of solution with benzene in a 125-ml. conical flask, evaporating most of the solvent to give a thin film over the lower half of the flask, and then warming the residue at about 0.5 mm. pressure in a 50° bath. The flask was weighed after successive 10 or 15 minute heating periods, and when the rate of weight loss (1–3% per hour) became constant, the extrapolated weight of the residue at zero heating time was taken as the weight of polyperoxide in the original sample. Some protection from light was necessary since the rate of weight loss was somewhat higher in diffuse light than from foil-covered flasks. A sample of 38 peroxide[2a] thus heated for 50 minutes, attained a constant rate of weight loss in 20 minutes. The final sample contained 1–2% benzene by infrared absorption at 6.75 μ. Higher temperatures resulted in higher steady rates of decomposition.

Anal. (Clark Microanalytical Lab.). Calcd. for $(C_8H_8O_2)_n$: C, 70.57; H, 5.92. Found: C, 71.0, 70.8; H, 5.7, 5.7. 70.9% C corresponds to 1.5% excess styrene or benzene in the polymer.

The 90–96% "purities" recorded for the peroxides used for most of the decompositions in Table I result partly from our failure to appreciate the need for small samples and thin films in peroxide assays until a late stage in this research. However, most of the styrene peroxide preparations contained a small percentage of polystyrene. Decomposition 112, using sodium methoxide, yielded 3% of the original polymer as a white powder precipitated by methanol. This polymer contained 90.0% carbon and had an intrinsic viscosity in benzene of 0.254. From the relation,[8] $\overline{M}_n = 167000\ [\eta]^{1.37}$, this polymer has a molecular weight of about 26,000. The carbon content corresponds to 96.5% polystyrene and 3.5% oxygen.

Determination of Styrene Peroxide.—The most reliable method of determining styrene peroxide was by isolation and combustion as indicated above. Infrared absorption, a hydriodic acid method,[2a] and a mercaptan method had limited usefulness; the acetic anhydride–sodium iodide method of Nozaki[9] was unsuitable except for the more reactive hydroperoxide end groups.[2a]

Styrene peroxide has weak characteristic absorption bands at 7.42, 10.97 and 11.15 μ. These bands disappeared on thermal decomposition, but they were so weak in comparison with strong adjacent bands of decomposition products that this method was little used. The peroxide has a stronger and broad absorption band at 9.75 μ. Since this band also appears in benzyl alcohol and phenylglycol, it may be used to follow the oxidation of styrene, but not the decomposition of the peroxide.

Determination of styrene peroxide with mercaptans is based on the reactions

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[7] W. Langenbeck, *Angew. Chem.*, **61**, 186 (1949), has reviewed this type of condensation.

[8] F. R. Mayo, R. A. Gregg and M. S. Matheson, This Journal, **73**, 1691 (1951).

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

$$\frac{1}{n}(\text{—OCH}_2\text{CHC}_6\text{H}_5\text{O—})_n + 2\text{RSH} \longrightarrow \text{HOCH}_2\text{CH(OH)C}_6\text{H}_5 + \text{R}_2\text{S}_2$$

$$2\text{RSH} + \text{I}_2 \longrightarrow \text{R}_2\text{S}_2 + 2\text{HI}$$

A mercaptan solution is standardized by titration with iodine in aqueous potassium iodide solution. An aliquot is then treated with styrene peroxide under standard conditions. The decrease in mercaptan content corresponds to the amount of mercaptan oxidized by the peroxide. With thiocresol, 79–82% of the theoretical mercaptan was uniformly oxidized, and this amount was insensitive to reaction conditions. The amount of peroxide found by titration was therefore muliplied by 1.25 to obtain the absolute amount present. In following the disappearance of peroxide in a decomposition, only the change from the initial titer was required. Except with benzyl mercaptan, addition of some base was required, leading to undesirable side reactions.

The other mercaptans tested, and the highest extents of reaction found with styrene peroxide were: β-mercaptoethanol, 30%; thioglycolic acid, 23%; thioacetic acid, 7% in 1 minute, 115% in 30 minutes; *p*-nitrothiophenol, 76%; thiophenol, 67%; benzyl mercaptan, 40%. With benzyl mercaptan, addition of base was not required for reaction, but results were erratic, with or without base. Although preliminary tests indicated that these mercaptans gave poorer results than thiocresol, conditions might be found where better results would be obtained. *p*-Nitrothiophenol and thioacetic acid seemed particularly sensitive to air oxidation, and benzyl mercaptan gave more consistent results in sealed tubes.

On the basis of numerous experiments, the following procedure was adopted for peroxide analyses with thiocresol. A 1 *M* solution of Eastman Kodak Co. *p*-thiocresol in benzene was prepared. Blanks were run on 1.00-ml. aliquots of this solution, using 0.1 *N* iodine in aqueous potassium iodide. Sodium thiosulfate was used for back titration when needed. Ten-ml. burets graduated to 0.05 ml. were employed. For a peroxide determination, 1 ml. of mercaptan solution was placed in a supported and tilted 24 × 120 mm. test-tube. One ml. of styrene peroxide solution, about 0.35 *M* (0.70 *N*) in benzene, 0.1 ml. of 0.2 *M* sodium methylate in methanol (or sodium ethylate in ethanol), 3 ml. of benzene and a tiny boiling stone were added in that order. This mixture was then refluxed over a small gas flame for two minutes, using the large test-tube as an air condenser. The reaction mixture was then washed into a 125-ml. conical flask, using 25 ml. of 65% methanol and 1–2% glacial acetic acid in water, and titrated with 0.1 *N* aqueous iodine solution. Starch could be used to improve the end-point, but was not necessary. The difference between the iodine consumed by the blank and by the analysis corresponds to mercaptan consumption and peroxide found. The proportions of reagents used are not critical, and benzaldehyde (except in large proportions), benzyl alcohol, phenylglycol and hydroxyacetophenone do not affect the determination of peroxide. However, benzoic acid (which is hard to exclude from benzaldehyde solutions) does interfere, and its effects can be largely offset by addition of more base. The presence of benzoic acid in benzaldehyde experiments was indicated by precipitation of sodium benzoate when sodium methylate was added to the reaction mixture. In the experiments titrated in 65% methanol, 0.1–0.2 ml. of glacial acetic acid was also present in each titration mixture, to remove alkalinity. No effect on the results was noticed, and duplicate determinations usually agreed within 1%.

The acetic anhydride–sodium iodide method of Nozaki[8] gave erratic results with styrene peroxide. No more than 70% of the theoretical iodine was liberated at temperatures from room to reflux. The difficulty lies in some side reaction: in experiments at 50°, the 65% limit of iodine liberation was reached in about one hour, and little further change occurred in the next three hours.

Identification of Products.—Analyses by infrared absorption were carried out with a model 21 Perkin–Elmer recording spectrograph, usually using 10% weight solutions in chloroform and 0.1-mm. absorption cells. Standard solutions of the following compounds were prepared for this work: benzene, styrene, α-methylstyrene, polystyrene, methanol, ethanol, benzyl alcohol, α- and β-phenethyl alcohols, phenylglycol, α-phenylglycerol, benzaldehyde, α-hydroxyacetophenone, acetophenone, benzil, benzoin, benzoic acid, phenylacetic acid, phenylglyoxylic acid, acetic anhydride, benzoyl chloride, methyl, isopropyl and benzyl benzoates, benzyl formate, benzyl acetate, α-acetoxyacetophenone, α-benzoyloxyacetophenone, benzylidene acetate, phenylglycol diacetate and dibenzoate, *meso*-diphenylglycol dibenzoate, methyl mandelate, dibutyl phthalate, *s*-trioxane, styrene oxide, phenylglycol methylene ether and α,α'-azodiisobutyronitrile. Many of these reference compounds were never found as products of styrene peroxide, but other unidentified compounds were found in many products.

Chloroform was chosen as standard solvent because phenylglycol, often an important product, was not readily soluble in carbon tetrachloride or carbon disulfide. Either of the latter would have been a better choice, however, because they have fewer absorption bands and no alcohol preservative. Any insoluble phenylglycol could have been isolated and determined separately.

Experimental Results

Thermal Decomposition.—Styrene peroxide is stable in the cold and dark. The rate of decomposition increases with increasing temperature and may become explosive above 100°. Tests on 0.05-g. samples as films in test-tubes showed that explosions occurred in about 20 seconds when the tubes were introduced into oil-baths at 130°, but none occurred at 115°. Explosions may depend on sample size, viscosity, and heat transfer, and are less probable when solvents are present or when gas is being evolved at low pressure. Gradual heating of the peroxide generates benzaldehyde which, as solvent, reduces the chance of an explosion. Only a portion of the sample may explode at one time, and when a small sample is placed in a gas flame, it sputters and disappears in a series of puffs.

Section A of Table I summarizes thermal decompositions of styrene peroxide. The major products are benzaldehyde and formaldehyde, and these become nearly the exclusive products in the fastest decompositions. The next most important product is α-hydroxyacetophenone. The yield of hydroxyacetophenone approached one-third of the aldehyde yield in lower temperatures or controlled decompositions. Rates of decomposition at 100°, determined by titrations of remaining peroxide with thiocresol, are summarized in Fig. 1. The rate in benzene solution is about the same as with no solvent, but the rate in α-methylstyrene solution is significantly slower. The rate changes in these decompositions corresponded roughly to a second-order reaction. The low final rate may be due to retardation by products. When these volatile products are removed continuously by vacuum distillation, the peroxide decomposition has about the same initial rate, but then proceeds rapidly to completion. However, the decomposition in benzene at 80° follows a first-order rate law within experimental error.

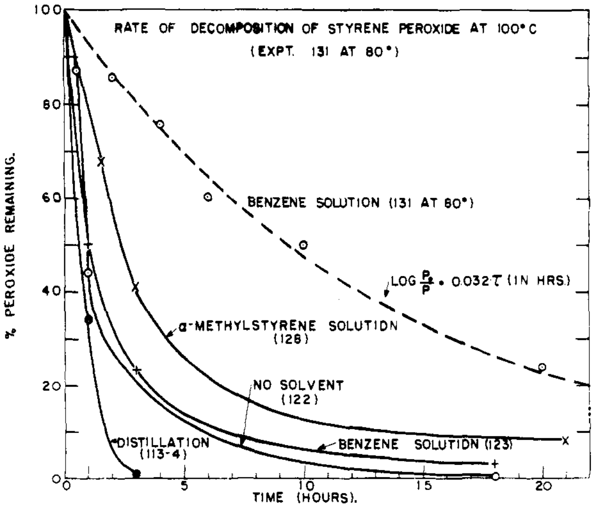

Fig. 1.—Rate of decomposition of styrene peroxide at 100° (expt. 131 at 80°).

Table II summarizes the earlier and final stages of expt. 123. The data show that the weak absorption bands corre-

TABLE I

DECOMPOSITIONS OF STYRENE PEROXIDE

	Peroxide							Products (mole %, if known, or weight %)						
Expt.	Wt., g.	Purity,[a] %	Solvent	Amt., g.	Other conditions	Temp., °C.	Time, hr.	BzH	Bz-CH_2OH	Phenylglycol	Unident. volatile[b]	Unident. non-vol.[b,c]	Recovered polymer[c]	Remarks
					A. Thermal decompositions									
114	2.11	90.5	None		Distn. at 0.001 mm.	100	1.0	37	6		9	47		28% CH_2O, 34% peroxide[t] in residue
113	2.04						3.0	55	10		12	17		34% CH_2O, 1%
122	0.63	90.5	None		Sealed, evac. tube	100	18							0.5% peroxide[t] left, *cf.* Fig. 1
56	3.92	93	None		Polymer spread out in long tube, heated to series of explosions at 0.2 mm. press.			93	0.4			4		84% CH_2O
A	2.8		C_6H_6	2.8	Soln. added dropwise to 100 ml. r.b. flask at 290–300° in stream N_2 (200 ml./min.)		0.5	64				4		
B	7.25	93.5	Styrene	21.7				79						36% CH_2O + 3.43 g. polymer containing 90.2% C
44	1.44	97.5	H_2O		Steam distilled	100	11.1	42				14		50% CH_2O
147	2.00	90.8	Bu_2 phthalate	18.0	Distn. at 0.2–3.0 mm.	100–145	0.25	66	20					
123	3.5	90.5	C_6H_6	31.5	Sealed, evac. tube	100	72	50	10					2.8% peroxide[t] left, *cf.* Fig. 1
131	4.0	90.5	C_6H_6	36.0	Sealed, evac. tubes	80	72	46	13					2.8%
							232	52	13					1.6%
71	5.0	93.5	BzH	10.0	Corked test-tube	80	10	12[e]	6		22		36	10% $C_6H_5CH_2OH$ + 9% BzOH
134	10.0	95.4	BzH	20.0	Sealed, evac. tube	80	43	24[e]	9		45	9	2	2% $C_6H_5(CHOBz)_2H$
150	5.0	90.8	C_6H_6 Bu_2O	30.0 35.0	Solvents distd. slowly	90–130	3.0	31	4	1		12	5	2.4% BzOH
154	3.25	90.8	Ac_2O	29.4	Sealed, evac. tube	100	6.0	16		<7*	>38	19	3	Products contain bound solvent
3	1.36	93.5	Styrene	2.08	N_2 atmos.	87	5.1							2.93 g. MeOH-insol. polymer, 83.6% C corresponds to 1.25 g. 93.5% peroxide in polymer
19	1.96	90.6	Styrene	34.4	Sealed, evacuated tube	80	21.5	38					38	3% CH_2O,[p] styrene completely converted to polymer containing peroxide residues
89	2.72	95.4	α-Methylstyrene	23.6	Sealed, evacuated tube	80	65	33	12	4	55		4	*Cf.* Fig. 1 products contain bound solvent
128	4.00			36.0		100	72	72	7	4	54			
87	2.72	95.4	Allyl acetate	20.0		80	65	48	7	3		59		
					B. Photodecompositions									
91	2.07	90.8	None		Sealed, evacuated Pyrex tube in intermittent sunlight	Room	12 days	34	18					

TABLE I (*Continued*)

Expt.	Peroxide		Solvent	Amt., g.	Other conditions	Temp., °C.	Time, hr.	Products (mole %, if known, or weight %)						Remarks
	Wt., g.	Purity,[a] %						BzH	Bz-CH_2OH	Phenyl-glycol	Unident. volatile[b]	Unident. non-vol.[b,c]	Recovered polymer[c]	
142	5.00	95.4	C_6H_6 Ac_2O	1.0 10.0	Sunlight, Pyrex flask	35–40	3.5	9			16	5	51	
59E	*x*	93.5	$CHCl_3$	9*x*	Sunlight, Pyrex tube	20	0.25	25						
158	4.71	97.7	C_6H_6	42.4	10 cm. from A-H4 mercury lamp, Pyrex tube	19	15	42						
157	6.02	90.8	α-Methylstyrene	24.1		16	1.8	0.6						No significant change in IR absorption
C. Decompositions by bases														
40	5.00	90.6	C_6H_6	20.0 ml.	0.19 ml. Et_3N added over 4.5 hr. as 10% soln. in C_6H_6	Reflux	5.1	24	3	10	19	34		29% CH_2O,[p] products contained combined amine and BzOH
73	5.00	95	C_6H_6	5.0	0.40 ml. Et_3N added over 2 hr.	2–5	17	13	8	31		29		
137	5.00	95.4	C_6H_6 MeOH	15.0 5.0	1.74 g. Et_3N added slowly as 10% soln. in C_6H_6	30	4	19	18	10	52			
108	5.05	90.5	C_6H_6	4.95	Peroxide in benzene added slowly to 5.43 g. Ac_2O + 3.66 g. Et_3N	30–35	3.5	0*	22*	10*	32	55		Material balance shows incorporation of reagents
139	5.00	95.4	C_6H_6 Ac_2O	1.0 10.0	2.06 g. Et_3N added slowly	25–30	14		30*	27*		23		
42	5.00	97.5	C_6H_6	20.0	2.6 g. piperidine added over 4 hr.	22–43 Room	4 4			8	52	50		Dist. contained 12% combined benzoic acid, also piperidine and N-hydroxypiperidine
43	5.00	97.5	C_6H_6	5.0	Peroxide soln. added slowly to 9.32 g. piperidine	5–15	0.5			14	59	15		Dist. contd. comb. benzoic and other acids, piperidine and/or N-hydroxypiperidine
118	5.00	95.4	C_6H_6	15.0	1.2 g. $EtNH_2$ added slowly as 10% soln. in C_6H_6	30–32	1			20	36			
149	5.00	90.8	C_6H_6	10.0	0.3 g. *t*-$BuNH_2$ added slowly as 10% soln. in C_6H_6	25–30 50 25	18.5 5.5 40	14	16	11		27	5	
168	20.0	97.7	C_6H_6	80.0	1.2 g. *t*-$BuNH_2$ added in 3 portions	25 50	59 40	20	13	10	50		7	Little or no reaction at 25°
	14.5	See remark	C_6H_6	85.5	0.15 g. *t*-$BuNH_2$, then 0.72 g. Et_3N	50 Room	21 120							All but recov. polymer above re-treated; little further change by infrared
70	5.00	93.5	C_6H_6	10.0	NH_3 passed through solution	24–8	6.5	16	12	14	55		1	
72	5.00	93.5	C_6H_6	5.0	0.05 g. 2-aminopyridine	60	10	37	6	5	11	32		
60	10.00	93.5	C_6H_6	20	20 ml. 1 *N* NaOEt (27 mole %) added slowly	1–4	2.2	23	3	19	3	10	19	7% BzOH, also unidentified acids
125	25.00	85.5	MeOH C_6H_6	15 ml. To 100 ml.	20 ml. 2 *N* NaOMe (~25 mole %) added over 2 hr.	30	2.8	24	2	13	1	14	13	5% BzOH, 3% HCO_2H, 2% other acids, 2% BzOMe, 2% Me mandelate

Table I (*Continued*)

	Peroxide							Products (mole %, if known, or weight %)						
Expt.	Wt., g.	Purity,[a] %	Solvent	Amt., g.	Other conditions	Temp., °C.	Time, hr.	BzH	Bz-CH_2OH	Phenyl-glycol	Unident. volatile[b]	Unident. non-vol.[b,c]	Recovered polymer[c]	Remarks
64	5.00	93.5	C_6H_6	5.0	Stirred with O_2 + 30 g. 20% aq. KOH; sudden temp. rise after 8 hr.	Room	72				8			14% BzOH, 3% mandelic acid, 11% unidentified acids, 26% benzyl alcohol
75	2.00	95.4	None		Distilled with 0.10 g. $Ca(OH)_2$ at 10^{-4} mm. press.	100	4	62	5			30		~60% CH_2O
124	5.00	95.4	C_6H_6 Ac_2O	3.0 20.0	1.0 g. fused NaOAc	100	16	<1	8*	14*	37	32		27% CH_2O,* 5% C_6H_5-CH-OAc-CO_2Na
					D. Decomposition by acids									
69	5.00	93.5	C_6H_6 AcOH	5.0 2.0	0.1 g. 1% $HClO_4$ in AcOH	60	8							
					addnl. 0.1 g. 1% $HClO_4$ in AcOH	60	6	28	2			10	60	
67	5.00	93.5	C_6H_6	5.0	0.10 ml. 1% $HClO_4$ in AcOH	80–90	1.7	75				22		2% CH_2O[p]
13	1.25	88.5	Ac_2O	To 25 ml.	0.10 ml. concd. H_2SO_4, CO_2 atm.	80–84	0.6	<5			66		29	Temp. reached 84° after 17 min. in 80° bath
81	5.00	95.4	C_6H_6 Ac_2O	2.0 8.0	0.5 ml. 2% p-$MeC_6H_4SO_3H$ in Ac_2O	100	8	10			9	37		55% benzylidene acetate
78	2.00	93.5	None		0.12 g. 85% H_3PO_4 at 10^{-4} mm. press.	76	0.8							
						87	1.0					80		
79	2.00	95.4	None		0.037 g. 85% H_3PO_4 at 10^{-4} mm.	109	3.3	60	3			35		
45	4.91	93	C_6H_6	5.1	2.0 g. AcOH	50	72	20			20		57	
93	2.04	90.8	None		0.20 g. BzOH	60	288	36	4		60			
					E. Reductions									
R2	4.3		C_6H_6 EtOH	50 ml. 50 ml.	0.2 g. PtO_2 + H_2 at 40 p.s.i.	25	6							No reaction
					C_6H_6 added to dissolve polymer	25	15	8	8	38	11	5	3	
R4	3.8		C_6H_6	10 ml.	0.20 g. Et_3N added slowly over 3 hr. at 0°, left 12 hr. at 0°, 0.1 g. each PtO_2 and 5% Pd on Al_2O_3 added; H_2 at 40 p.s.i.	25	15		9	~60	16	8		
172	20.0	96	C_6H_6 EtOH	60.0 60.0	40–50 p.s.i. H_2; 3.0 g. Ni^d + 1.0 g. t-$BuNH_2$	25–37	2.0		3	65		10		8% benzyl alcohol
173					1.2 g. Ni^d + 0.35 g. t-$BuNH_2$	25–36	2.5		6	51		21	1	7% benzyl alcohol
174					1.2 g. Ni^d + 0.70 g. t-$BuNH_2$	25–37	2.0	0.6	9	58		11		6% benzyl alcohol + 0.4% BzOH
175	20.0	96	C_6H_6 EtOH	60.0 60.0	40–50 p.s.i. H_2; 3.05 g. Ni^d + 0.35 g. t $BuNH_2$	25–39	3.3			81		3		8% benzyl alcohol
176					3.05 g. Ni^d	25–29	2.0							Only 55% of final H_2 absorbed
					0.14 g. t-$BuNH_2$	25–29	1.0			80		2		5% benzyl alcohol
177					3.00 g. Raney Ni + 0.35 g. t-$BuNH_2$	26–35	7.3							93% of final H_2 absorbed
					0.35 g. t-$BuNH_2$	27–29	4.4	0.4	6	58		7		16% benzyl alcohol

Table I (*Continued*)

	Peroxide							Products (mole %, if known, or weight %)						
Expt.	Wt., g.	Purity,[a] %	Solvent	Amt., g.	Other conditions	Temp., °C.	Time, hr.	BzH	Bz-CH_2OH	Phenylglycol	Unident. volatile[b]	Unident. non-vol.[b,c]	Recovered polymer[c]	Remarks
R6	3.4		C_6H_6	25 ml.	Peroxide added over 2 hr. to 15 ml. 50% by wt. dispersion of Na in toluene	Room	16			14	10	30		
119	10.0	95.4	C_6H_6 *i*-PrOH	10.0 40 ml.	7.5 g. Al(O-*i*-Pr)$_3$, 50 mole %	Reflux	90			10	13	23		27% benzyl alcohol 8% α-phenylglycerol
63	5.03	93.5	C_6H_6	1.04	15.96 g. phenylhydrazine	Room	144			16–24				11–29% $C_6H_5CH{=}N{-}NHC_6H_5$ 2–12% $C_6H_5(C{=}N{-}NHC_6H_5)_2H$
62	5.96	93.5	C_6H_6 EtOH	11.92 2.0	H_2S added continuously 0.4 millimole (1 mole %) NaOEt in EtOH added in 4 portions over 3 hr.	30–50	16	4	5	64				0.74 g. S + 1.01 g. (S + distillation residue)
169	10.0	97.7	C_6H_6	10.0	Peroxide soln. added over 2 hr. to 5 millimoles (6.8 mole %) NaSH in 15 ml. EtOH + 20 ml. C_6H_6 in stream H_2S	30	3.8	5	3.5	69		3		1.89 g. (80% theor.) S
					F. Miscellaneous decompositions									
97	5.00	90.8	C_6H_6	10.0	0.10 g. 5% Pd on Al_2O_3	Reflux	4.7	50	5		19		6	
160	5.00	97.7	Dibutyl phthalate	10.0	Peroxide in half of phthalate added slowly to rest of ester + 0.1 g. 5% Pd on Al_2O_3 over 75 min. at ~0.001 mm. press.	100–105 105–119	0.75 0.3	47	9					
141	5.00	95.4	C_6H_6	20.0	1.0 g. 10% Br_2 in C_6H_6 added over 2 hr. in sunlight	35–40	3	44			28	12	2	
146	5.00	90.8	C_6H_6 Ac_2O	2.0 15.0	1.48 g. 10% Br_2 in C_6H_6 added slowly in sunlight	27–37	2	8				5	51	
86	5.00	95.4	C_6H_6	10.0	0.10 g. manganous stearate	25–80 80	1.7 16	54	3	3	17	22		45% CH_2O[p]
85	5.00	95.4	C_6H_6	10.0	0.10 g. ferric stearate	25–80 80	1.7 0.8	74				21		18% CH_2O,[p] fast reaction after 20 min. at 80°
100	2.06	90.8	None		0.010 g. ferric stearate at 10^{-4} mm. pressure	76	7.5	72	6	4		13		
138	5.00	95.4	C_6H_6 Ac_2O	1.0 10.0	0.25 g. I_2, sealed, evac. tube	100	24	63*	8*	10*		34		13% CH_2O*
76	5.00	95.4	C_6H_6	5.0	Satd. with SO_2 0.2 g. Et_3N added as 10% soln. in C_6H_6, warmed gradually to 60°	Room 60	23 19						93	5% water-soluble material found

[a] Purity is based on carbon analyses, assuming that polymer consists only of $C_8H_8O_2$ units and excess styrene. Yields are calculated as if the polymer were pure $C_8H_8O_2$, and so the excess styrene should be found as unidentified material or recovered polymer. [b,c] A figure between these columns indicates that no separation was effected. [d] Modified Raney-type nickel.[5a] [e] BzH yields are increase over original BzH. [p] Paraformaldehyde found; unknown amount of monomeric aldehyde lost. [t] By titration, thiocresol method. * As acetyl derivative.

sponding to styrene peroxide disappear faster than titratable peroxide, suggesting that these bands are not characteristic of low molecular weight peroxide. The formations of benzaldehyde and hydroxyacetophenone lag behind the disappearance of titratable peroxide. Perhaps hydroxyacetophenone is an end-product of several rearrangements of hydrogen atoms and is partly consumed in secondary reactions. In any event, the benzaldehyde concentration continues to increase after substantially all the peroxide has decomposed and there is simultaneously a general increase in infrared absorption which must be due to secondary reactions. Similar changes occurred more slowly at 80°.

TABLE II

DECOMPOSITION OF 10% SOLUTION OF STYRENE PEROXIDE IN BENZENE AT 100°

See expt. 123 in Table I for final results.

Reacn. time, hr.	Original peroxide remaining by titration, %	Ultimate change in infrared Absorption, % 7.4μ	Peroxide 11.0μ	11.2μ	BzH 12.1μ	BzCH₂·OH 10.3μ
1	50.0	60	54	62	47	31
3	23.5	100	100	100	69	60
18	3.2	..	..	..	91	102
72	2.8	..	..	..	100	100

The cleanest decomposition (expt. 56) giving 80–95% yields of benzaldehyde and formaldehyde, was obtained by exploding the peroxide at low pressure. When the polyperoxide was spread out in a large Pyrex tube, heating with a gas flame resulted in mild explosions which did not affect unheated peroxide. The abnormally low proportion of hydroxyacetophenone suggests that this explosive decomposition is largely a chain reaction leading to the two aldehydes. Good yields of aldehydes may also be obtained by flash decomposition of peroxide solutions (expts. A and B). The three runs last mentioned represent first trials and better yields and material balances can probably be obtained. Steam distillation (expt. 44) also gave a clean decomposition from the standpoint of small quantity and light color of the residue, but recoveries of products were poor. Distillation of the peroxide as a 10% solution in dibutyl phthalate (expt. 147) gave the best yield of hydroxyacetophenone. This ester was chosen because it boils just above hydroxyacetophenone and phenylglycol, so that these products would be removed rapidly. Slower distillations gave less hydroxyacetophenone.

The decompositions of styrene peroxide in benzaldehyde as solvent demonstrate that this aldehyde participates in the decomposition and complicates decompositions in which it is not constantly removed. At 100° the decomposition is only slightly faster in benzaldehyde than in benzene: recoveries of methanol-insoluble polymer after heating 10% solutions of peroxide for one hour at 100° were 56% from benzene, 43% from benzaldehyde. Experiment 71 shows that decomposition is not rapid at 80°, and a longer run (134) gave a large amount of unidentified material which resembled that formed in the photodecomposition of benzaldehyde alone.[10] Investigation of the high-boiling products yielded 3 g. of liquid distilling at 180° at 1 mm. pressure. Its infrared absorption suggested a mixture of ester with aldehyde or ketone. Although this fraction could not contain free benzaldehyde, treatment with 2,4-dinitrophenylhydrazine and hydrochloric acid in methanol gave benzaldehyde dinitrophenylhydrazone corresponding to 30% benzaldehyde in the fraction. Saponification with sodium hydroxide in aqueous alcohol gave benzoic acid and phenylglycol corresponding to 25 and 20% of the fraction (and to considerably more monophenylglycol dibenzoate than could be found by infrared absorption). No diphenylglycol dibenzoate was found, but a trace of the *meso* isomer was isolated from a similar experiment.

Pilot decompositions in dibutyl ether (expt. 150) or acetic anhydride (expt. 154) as solvents showed no clean reactions and were not investigated further.

Styrene peroxide accelerates the polymerization of styrene and is partly incorporated in the new polymer. Carbon analyses of polymer fractions show that these range from polystyrene to polyperoxide, and it seems probable that both large and small fragments of peroxide molecules may be incorporated in the polystyrene. Recovery of some peroxide in expt. 19 shows that peroxide links are not readily attacked by styrene radicals in the presence of styrene monomer. α-Methylstyrene is also a good trap for peroxide radicals. Almost all the methanol-soluble products in expt. 89 distilled at 38–190° at 5 mm., and since they contained only 75.7% carbon, they could not contain very much bound α-methylstyrene. The rather high ratio of hydroxyacetophenone to benzaldehyde suggests that most of the aldehydes came from chain decomposition, here retarded, while the hydroxyketone arose from disproportionation. Experiment 128 at 100° apparently gave more chain decomposition at the higher temperature. Here the highest boiling distillate and residue had infrared absorption closely resembling that of α-methylstyrene. Since they could contain no monomer, 2,5-diphenyl-1,5-hexadiene is a possible product. Although allyl acetate was partly polymerized by the peroxide, not enough copolymerization of allyl acetate with styrene peroxide units occurred to be interesting.

Oxygen has little effect on the decomposition of styrene peroxide. When 0.10 g. samples of peroxide were heated gradually in atmospheres of oxygen or nitrogen, both exploded almost simultaneously at a bath temperature of 115–120°. Five per cent. solutions of styrene peroxide in acetic anhydride were heated to 80° for 2 days in slow streams of oxygen or nitrogen, and the rates of peroxide disappearance were followed by titration. The decomposition in oxygen was about five-sixths as fast as in nitrogen over the whole time. A somewhat larger difference between the two gases has been found with α-methylstyrene.[2b]

Photodecompositions.—The photodecomposition of styrene peroxide has been studied in Pyrex vessels under various conditions, using both sunlight and a mercury arc. Section B of Table I shows that the photolysis is fast in chloroform, moderate in benzene and acetic anhydride, and very slow in α-methylstyrene solution. The only products identified in these runs were benzaldehyde and formaldehyde. In benzene runs, the course of the reaction was followed by infrared absorption. The formation of benzaldehyde corresponded closely to the disappearance of peroxide, but degraded, methanol-soluble peroxide which contained hydroxyl and carbonyl groups was also formed. Presumably, the primary products of photolysis are alkoxy radicals from the weak peroxide bond. Disproportionation reactions of these alkoxy radicals produce the hydroxyl and carbonyl groups while the unimolecular reactions of the same radicals produce the aldehydes. In photolyses with solvents, significant but variable yields of hydroxyacetophenone were produced. In viscous reaction mixtures disproportionation of the initially formed alkoxy radicals may be favored, and hydroxyacetophenone results from two such reactions on each side of a styrene unit. Periodic removal of formaldehyde gas by evacuation, or addition of benzoic acid, seemed not to affect the yield of hydroxyacetophenone in solvent-free experiments.

The effects of solvents, retarders and temperature were investigated more carefully on a sample of styrene peroxide analyzing for 1.05 C_8H_8/O_2 and having a cryoscopic molecular weight of 2260 in benzene; 20–30 ml. of peroxide solutions, 0.5 *M* in peroxide units, in Pyrex test-tubes, were irradiated 10–15 cm. from an A-H4 mercury lamp, with a 6-mm. Pyrex filter interposed. Nitrogen was bubbled slowly through the solutions to provide agitation and exclude oxygen. Three-ml. samples were removed periodically and analyzed for benzaldehyde with dinitrophenylhydrazine. Results are summarized in Fig. 2. Because of variations in reaction tubes and tube-lamp distance, some data are comparable, but others are not. The quantum yield for 0.5 *M* peroxide in benzene was 5.0–5.2 at 27–28°, proving the chain

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[10] 5.12 g. of benzaldehyde was exposed to sunlight in a sealed, evacuated Pyrex tube for 7 weeks. A few crystals separated (0.04 g.) and were identified as *meso*-diphenylethyleneglycol dibenzoate. 3.20 g. of aldehyde was recovered and 1.86 g. of non-volatile or slightly volatile residue was obtained. The residue had an infrared absorption much like that of the crystalline dibenzoate and probably contains some of the non-crystalline racemic isomer. The residue did not contain much benzoic acid, monophenylglycol or its dibenzoate, or benzil, and contained less than 10% benzoin (if any). The diphenylglycol dibenzoates have been obtained in good yield from di-*t*-butyl peroxide and benzaldehyde by Rust, Seubold and Vaughan, THIS JOURNAL, **70**, 3258 (1948).

nature of the photolysis. Some details of this measurement are at the end of this section.

Two of the 50° experiments show that, in comparison with benzene, styrene as solvent retards photolysis. By analogy with results with α-methylstyrene and its polymeric peroxide, the retardation is due to a chemical, rather than a filtering effect of the solvent.[2b] Perhaps, nearly all the alkoxy radicals add to styrene (or α-methylstyrene, expt. 157) before they can release benzaldehyde or formaldehyde.

Two other experiments show how the initial rate of photolysis increases with temperature over the range 25–50°. Other experiments with 1 M peroxide in toluene at +20° and −75° suggest that, at the lower temperature, photodissociation is nearly as fast as at room temperature, but that the alkoxy radicals disproportionate to hydroxyl and carbonyl compounds rather than split out aldehydes. As measured by decrease in viscosity, the cleavage was about half as fast at −75° as at +20°. However, the rate of formation of benzaldehyde was no more than 15%, and possibly only 5%, as fast at the lower temperature. The dinitrophenylhydrazone obtained from the low-temperature photolysis melted from 150–230° in contrast to the pure benzaldehyde derivative (m.p. 234–237°) obtained in other experiments.

Figure 2 also shows that hydroquinone inhibits photolysis at room temperature while thiophenol does not. The hydroquinone is apparently converted to quinone in the process; the solution acquired a yellow color but irradiated solutions of the individual reagents did not. It may be inferred that the phenylmercaptyl radical, but not the p-hydroxyphenoxy radical, attacks the styrene peroxide and continues reaction chains.

All these data on photodecompositions suggest that the chain decomposition of alkoxy radicals into aldehydes requires more activation energy than the reaction of the same radicals with each other (disproportionation), with reactive double bonds (styrene and α-methylstyrene) or with active hydrogen donors (thiophenol or hydroquinone). Thermal experiments in section A also pointed to more chain decomposition at higher temperatures.

Quantum yields for styrene peroxide were determined by uranyl oxalate actinometry in a compound reaction cell similar to that described by Noyes and Leighton.[11] The solutions were placed in 1-cm. absorption cells about 20 cm. from an A-H4 mercury lamp, and a 6-mm. Pyrex filter was placed between the lamp and the cells. Measurements are therefore based on weak absorption of wave lengths greater than 3000 Å., while styrene peroxide begins to absorb strongly only below 3000 Å. A nitrogen atmosphere was kept over the non-thermostated cells, and a correction was made for the light absorption by benzene. A two-hour experiment at 27° gave 5.0 molecules of benzaldehyde per quantum absorbed by the peroxide. A four-hour run at 28° gave a quantum yield of 5.2.

Decomposition by Bases.—The best support for the conclusion that disproportionation is the primary reaction comes from expt. 139 (section C of Table I) where acetic anhydride was employed to acetylate and stabilize the hydroxyacetophenone. The 30% yield of this product was the highest obtained in any decomposition of styrene peroxide. On a purely statistical disproportionation, 15% each of phenylglycol and phenylglyoxal should accompany 30% hydroxyketone. The 27% yield of glycol may be partly due to the reducing action of the amine.

In expt. 40, 5 mole per cent. of triethylamine, added in small portions to the peroxide in refluxing benzene, was sufficient to cause nearly complete decomposition of the peroxide. Reaction at this temperature gave the most aldehydes, and paraformaldehyde collected in the condenser. The distillate fraction contained phenylglycol, and an amine and benzoic acid were found on treatment with base and acid, respectively. When the triethylamine-catalyzed decomposition was carried out at 2–5°, more hydroxyacetophenone and phenylglycol and fewer cleavage products (aldehydes) were formed. The decreased cleavage at lower temperatures suggests that at least some cleavage results from interaction of hydroxyacetophenone with amine. Dilute alkalies (as well as acids and hot water) are reported to effect the cleavage of hydroxyacetophenone to benzaldehyde and formaldehyde.[12] Use of methanol as solvent (expt. 137) also improved the yield of hydroxyacetophenone.

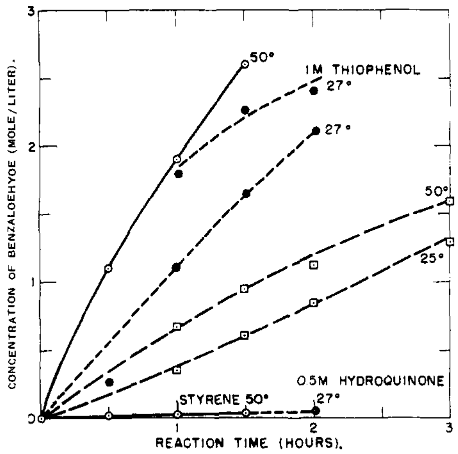

Fig. 2.—Photolysis of 0.5 M styrene peroxide at 25–50° in benzene as solvent (except where styrene is indicated). Only lines with similar breaks are directly comparable.

Although piperidine readily caused decomposition of styrene peroxide, the amine was rapidly destroyed and about one-half mole was required per peroxide unit. Both piperidine and N-hydroxypiperidine were found combined with benzoic acid in the products, suggesting oxidation of both piperidine and of benzaldehyde. Ethylamine seemed to behave like piperidine. t-Butylamine, which has no α-hydrogen atoms and is therefore less likely to be attacked by alkoxy radicals, showed more promise, but was not investigated adequately. Ammonia may be equally useful. 2-Aminopyridine in small proportions was still less effective; it had been hoped that this bifunctional compound, which readily effects proton transfer in glucose,[13] would act similarly with the peroxide.

Stronger bases than amines cause faster decomposition of peroxide and also more secondary and disproportionation reactions of primary products. Recoveries are often poor because of the high solubility of phenylglycol and some acids in water, and their low solubility in some organic solvents. In expt. 125, base was added regularly and aliquots were withdrawn for the determination of remaining peroxides and of free base (phenolphthalein). The data show a regular decrease in peroxide concentration with addition of base, a gradual increase in free base to a maximum of 0.02 N, but no change in peroxide concentration during the final 0.8 hr. while the free base concentration dropped to 0.01 N. These results are taken to mean that the reaction products are more sensitive than peroxide to the action of base and, since free base concentration rose gradually, some portions of the peroxide may be more sensitive than others to the action of base. Many experiments were carried out in an effort to obtain cleaner reactions, but without marked success. Aqueous alkalies reacted slowly because of immiscibility of base and peroxide, and the results suggest that a Cannizzaro reaction took place when enough benzaldehyde or benzyl alcohol[14] accumulated. Lime water caused little reaction in several days at room temperature. On the promise that hydroxyacetophenone is a primary product which might be obtained in improved yields by protecting it from base, distillations at low pressure from calcium hydroxide, or from a mixture of sodium acetate and acetic anhydride were tried. The first method still seems sound, but apparently failed because the base did not noticeably accelerate the decomposition. The second procedure was partly successful, but sodium acetate was less effective than triethylamine.

Reactions with triethylamine or sodium alkoxides were difficult to reproduce. The temperature of the stirred reaction mixture indicated whether reaction was occurring and how fast reagent should be added. Particularly with triethylamine, rather rapid reactions might occur without warning, as if an induction period were involved. While

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[11] W. A. Noyes and P. A. Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 82.

[12] T. Zincke, *Ann.*, **216**, 311 (1883).

[13] C. G. Swain and J. F. Brown, Jr., THIS JOURNAL, **74**, 2534, 2538 (1952).

[14] M. S. Kharasch and R. H. Snyder, *J. Org. Chem.*, **14**, 819 (1949).

it seems probable that experimental conditions and yields in section C could be improved, such a study seemed unlikely to yield much information about primary reactions of the peroxide.

Decompositions by Acids.—Decompositions of styrene peroxide in the presence of acid are summarized in section D of Table I. In all cases, the principal products identified were formaldehyde and benzaldehyde. With a dilute solution of perchloric acid in acetic acid as catalyst, and benzene as solvent for the peroxide, the decomposition at 60° proceeded to the extent of only about 30% in 14 hours (expt. 69). A similar mixture, on heating to 80°, gave such rapid decomposition that overheating and loss of benzene occurred (expt. 67). A phenol test on the products was negative. In a mixture like expt. 67, with about 50 times as much perchloric acid as catalyst, the peroxide on standing 3 weeks at room temperature gave 0.6% of a dark red-brown polymer. This polymer was insoluble in boiling benzene, did not melt below 280°, analyzed for only 51.9% carbon, and burned with a burst of sparks. Sulfuric acid and *p*-toluenesulfonic acid were less effective than perchloric acid in catalyzing decomposition of peroxide. With the sulfonic acid, benzaldehyde was apparently the major product but was largely acetylated to benzylidene diacetate in acetic anhydride solution.

Four experiments were carried out in which the peroxide was distilled at low pressure from small proportions of phosphoric acid into a liquid nitrogen trap, with the idea that primary products would thus be quickly removed. Experiment 78 shows that the reaction proceeds slowly near 80°. A similar mixture exploded violently after 10 minutes at 100°. With less phosphoric acid at 100° (expt. 79), the reaction volatilized slower than with no added acid (Fig. 1).

Acetic and benzoic acids exhibited little catalytic effect on the decomposition. Hydrogen chloride in benzene and methanol at room temperature gave tar.

Reductions.—In agreement with the experiments of Barnes and co-workers,[4] early attempts to reduce styrene peroxide catalytically to phenylglycol gave yields below 40%.[15] It was then found (section E of Table I) that addition of piperidine before reduction, or degradation of the peroxide with triethylamine (until the peroxide was no longer precipitated by methanol, expt. R4) resulted in yields of about 60%. Finally, five very similar experiments (172–176) were carried out with a modified Raney-type nickel catalyst[5a] and *t*-butylamine (which is not readily attacked by styrene peroxide). These experiments indicate that, in the solvent mixture employed, a relatively large quantity of catalyst (~15%) and a small proportion (~1%) of amine are desirable to obtain the best yields. Among the three experiments with 3.0 g. of catalyst, the initial rate of hydrogen uptake depended on the amount of amine present. Experiment 172 reached the indicated maximum temperature in 7 minutes, whereupon the reaction flask was cooled. Reduction expt. 176, with no amine, had practically ceased just before amine was added. The distillates in all of these experiments appeared to contain *t*-butylammonium benzoate. It is not clear whether the principal function of the amine is to degrade the polyperoxide, activate the catalyst or neutralize acid by-products, but an amine improves yields with platinum, palladium or nickel catalysts. Experiment 177 showed that commercial Raney nickel was less effective than the modified catalyst prepared in this Laboratory.

Reduction by a fine sodium dispersion (expt. R6) gave only 14% of glycol. Similar results were obtained at 0°, and with sodium hydride as reducing agent at 55–60°. With a deficiency of aluminum isopropoxide as reducing agent at 80°, the principal identified product was benzaldehyde. None of the expected methyl benzoate or benzyl formate was formed. With 50% excess of reducing agent (expt. 119), a small yield of phenylglycerol was found in addition to benzyl alcohol and phenylglycol. A gel containing 25% Al_2O_3 (after extraction and drying) was also isolated. The glycerol had an infrared absorption spectrum essentially identical with known 1-phenylglycerol. The 2-isomer is unknown.

Phenylhydrazine reacted slowly with styrene peroxide. The ranges in yields represent the pure and crude products formed. The data suggest that phenylhydrazine reacts as base (to cleave peroxide), as hydrogen donor (to produce glycol), and possibly also as oxidizing agent (to produce osazone).

Sulfhydryl compounds are particularly effective in reducing styrene peroxide to phenylglycol, but the reaction is not quantitative. Some base is required to maintain the reaction. β-Mercaptoethanol reacted in benzene solution to give water-soluble products. Thiophenol and several substituted thiophenols reacted completely on short refluxing in benzene and ethanol containing small proportions of sodium ethylate, but only 50–80% of the theoretical mercaptan was oxidized to disulfide. Several reductions by hydrogen sulfide were attempted before catalytic reduction was found more useful. Experiments 62 and 169 represent the more successful efforts. The products obtained suggest that the required base causes some cleavage of peroxide to hydroxyacetophenone and then to aldehyde. Some of these experiments yielded stiff resins with low solubility in both benzene and acetone. One resin analyzed for 24.1% C, 2.6% H, and 67.4% S, corresponding approximately to $[(C_8H_8)S_8O]_n$.

Miscellaneous Decompositions.—Section F of Table I summarizes numerous unsuccessful attempts to cleave styrene peroxide to hydroxyacetophenone, phenylglycol and phenylglyoxal with materials which might effect oxidation–reduction reactions by transfer of hydrogen atoms in the polymer. The principal products obtained were benzaldehyde and formaldehyde, with not over 10% of any other known decomposition product.

Most trials were made with a 5% palladium-on-alumina catalyst (Baker and Co., Inc., Newark, N. J.). When the materials were heated without solvents at reduced pressure, explosions occurred. Benzaldehyde and formaldehyde were the principal products collected before the explosion. Experiments 97 and 160 show that while the catalyst accelerated the thermal decomposition in solution, it had no marked effect on the products except possibly to decrease the yield of hydroxyacetophenone. Several experiments were tried with small amounts of bromine in sunlight with the idea that hydrogen bromide might serve as oxidation–reduction catalyst. Although some very fast decompositions could be obtained in benzene solution if the temperature was uncontrolled, the sole identified products were formaldehyde and benzaldehyde. When acetic anhydride was employed as solvent to protect any intermediate, the decomposition was retarded. These experiments indicate again that acid-catalyzed decompositions yield aldehydes.

Although manganous stearate (expt. 86) had little effect, ferric stearate caused a fast decomposition, but no unusual products (expts. 85, 100). Iodine in acetic anhydride had slight effect; the usual thermal products were acetylated. In a similar experiment, 75% of the original peroxide was recovered after 91 hours at 50°. Experiment 76 shows that sulfur dioxide not only failed to decompose the peroxide, but that it stabilized the polymer against the combined effects of heat and triethylamine.

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(15) These experiments, and those designated "R" in section E of Table I, were carried out by Dr. G. A. Russell.