rapidly with bromine in carbon tetrachloride with the evolution of hydrogen bromide, and polymerized on standing. Although the chemical properties correspond to a methoxystyrene, the boiling range indicates a mixture of products.

Summary

1. p-Iodostyrene has been prepared in a three step synthesis from p-aminoacetophenone.

2. A new synthesis for p-nitrostyrene from β-phenylethyl bromide has been developed.

3. α-Vinylthiophene has been prepared by the reaction of α-thienylmagnesium bromide with vinyl chloride in the presence of cobaltous chloride.

4. New physical constants are reported for p-nitro- and p-dimethylaminostyrene.
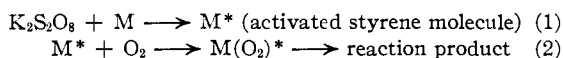

The Mechanism of Emulsion Polymerizations. III. Oxygen as a Comonomer in the Emulsion Polymerization of Styrene[1]

BY F. A. BOVEY AND I. M. KOLTHOFF

From previous studies,[1a] using the bottle technique, it was found (a) that the induction period caused by oxygen in the emulsion polymerization of styrene is approximately inversely proportional to the concentration of potassium persulfate used as "catalyst," (b) that the induction period is proportional to the amount of oxygen initially present, provided that the initial oxygen pressure is constant, and (c) that the length of the induction period is almost independent of the amount of soap in the charge. From experiments carried out at different initial oxygen pressures, it was further found that for a given amount of oxygen the induction period is somewhat dependent upon the initial oxygen pressure, i. e., that the rate of oxygen disappearance is evidently not quite independent of the oxygen partial pressure in the bottle.

From the fact that the length of the oxygen induction period is nearly independent of the amount of soap in the charge, it was inferred that the main locus of initiation of activated styrene molecules by persulfate is the true water phase and not the soap micelle.

It was postulated that the initiation reaction and the absorption of oxygen were related as shown in (1) and (2)

$$K_2S_2O_8 + M \longrightarrow M^* \text{ (activated styrene molecule)} \quad (1)$$
$$M^* + O_2 \longrightarrow M(O_2)^* \longrightarrow \text{reaction product} \quad (2)$$

The first reaction was presumed to be slow, and was regarded as the rate-determining step, whereas the second reaction was presumed to be very rapid. This mechanism requires, however, that the rate of disappearance of oxygen be independent of the oxygen pressure. The apparent failure of the oxygen disappearance to follow exactly a zero order law might be due to the relatively ineffective mixing of the liquid and gas phases under the conditions of these experiments, which

were carried out in 8-oz. bottles rotated end-over-end at about 35 r. p. m. In the previous work the rate of disappearance of oxygen was estimated from the length of the induction period with the assumption that no normal polymerization occurs in the presence of any oxygen in the system. It appeared desirable to make direct measurements of the rate of oxygen disappearance during the induction period in order to establish whether this rate corresponds to a zero order reaction when the system is stirred efficiently. Under the same experimental conditions the relation between the rate of oxygen uptake on the one hand and the concentration of soap and/or persulfate on the other could be determined.

In addition, we have isolated and studied the properties of the reaction product which is formed during the induction period in the presence of oxygen.

Experimental

Materials

Styrene.—Dow styrene with a purity of at least 99.5% was used. This material was distilled in vacuo just before use, although it may be safely stored for one or two days at 0–10°.

Water.—Conductivity water was used throughout.

Emulsifier.—Commercial soap (S. F.) flakes supplied by Procter and Gamble were employed. This material is largely composed of the sodium salts of stearic, palmitic and oleic acids, and contains only very small amounts of soaps of polyunsaturated fatty acids. The same lot of this material was used in all this work.

The sodium linoleate employed in Run 1, Fig. 3, was prepared from a sample of linoleic acid supplied by Dr. W. C. Ault of the Eastern Regional Laboratories.

Potassium Persulfate.—Merck reagent potassium persulfate, especially purified "for D. D. Van Slyke's Micro-Kjeldahl determination of nitrogen" was found to be satisfactory. It gave the same results as a product twice recrystallized from conductivity water.

Polymerization Recipe.—The following recipe, in which the amounts of several of the constituents were varied systematically, was used:

Styrene: 50.0 g. (55.2 ml. at 25°), designated as 100 parts.

Water: 90.0 g., or 180 parts, in separate portions of which the soap and catalyst were dissolved.

Soap: 2.50 g., or 5 parts based on styrene. This quantity of emulsifier will be denoted as "1-X," and other amounts as fractions or multiples thereof.

Potassium persulfate: 0.150 g. or 0.3 part based on styrene. This quantity of persulfate will be denoted as "1-X," and other amounts as fractions or multiples thereof. (Thus "5-X" means 1.5 parts per 100 of styrene.)

All work was carried out at 50.0 ± 0.2°.

A. Experiments Carried out in Magnetically Stirred Reaction Vessel

Technique.—These experiments have been carried out in an apparatus so designed that either a known volume of oxygen can be allowed to react with the styrene–water emulsion, and the decline in pressure followed, or the rate of reaction of the oxygen at a constant pressure can be measured.
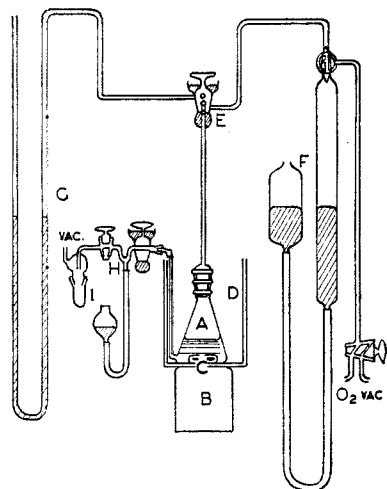

Fig. 1.—Magnetically stirred reaction system for measurement of oxygen consumption: A, reaction vessel; B, stirring motor; C, stirring magnet; D, water-bath; E, three-way mercury-sealed stopcock; F, gas buret; G, manometer; H, sample line with mercury seal; I, sample vessel.

The experiments described in this section were carried out in an apparatus (Fig. 1) that consisted of a 250-ml. Erlenmeyer flask surrounded by a constant temperature bath and attached by means of a standard taper joint to an open-end manometer. (A three-way mercury-sealed stopcock was provided in the line to the manometer so that the reaction vessel might be attached to a gas buret for work at constant pressure.) In order to eliminate any uncertainty as to seals, stirring was effected by means of a commercially available magnetic stirring device. This consisted of a motor which rotated a strong permanent bar magnet as close to the bottom of the reaction vessel as possible. Within the vessel, stirring was provided by a small piece of magnetized soft iron covered with Pyrex glass. This agitator is in the shape of a cylinder flattened on one side, and as it rotates with the rotating magnetic field impressed upon it from outside, apparently efficient stirring action results, producing a deep vortex.

Sampling could be accomplished during the course of the reaction without changing the pressure. This was done by means of a 1-mm. capillary tube leading from the bottom of the reaction vessel over the top of the bath to a sample container which was attached to the sample line by means of a standard-taper joint in such a way that when the pressure in the sample vessel was reduced (by means of a water pump) below the pressure within the reaction vessel, a portion of the reaction mixture flowed into the sample container. The flow was controlled by two stopcocks, the one nearest the vessel being sealed with mercury. The capillary between the stopcocks, which was of a U-form, was likewise filled with mercury, the level of which was controlled by a small leveling bulb. These precautions were found to be necessary if a static vacuum was to be maintained over a period of several hours. In carrying out a run, the styrene and aqueous solutions were first pipetted into the reaction vessel. The soap solution was pipetted in at 50°, the catalyst solution was pipetted in at 25°, and the styrene was added from a buret at 25°. The reaction vessel was then fitted to the ground-glass joint leading to the manometer, care being taken not to mix the oil and water layers. The thermostat bath was then put in place, and filled with water at room temperature. After allowing a few minutes for the contents of the vessel to cool somewhat to avoid excessive foaming, vacuum was applied to the flask by means of a water pump. When the pressure reached 50–75 mm., it was restored to atmospheric by introducing oxygen through the sampling line. This process was repeated four times, effectively replacing the air initially present by oxygen. The volumes of flask and manometer were accurately known, as well as that of the liquids charged. The temperature of the bath was then rapidly raised to 50° (ten minutes), the pressure equalized to the atmosphere, and agitation started. There was always an initial rather rapid drop of 10–20 mm. pressure, after which the pressure declined at a smaller rate. Readings of the manometer were taken every five to thirty minutes, depending upon the rapidity of the pressure decrease. In calculating the pressure of oxygen, correction was made for the vapor pressures of water and styrene, totaling 117 mm. at 50°. Ten-ml. samples were taken from the reaction mixture at appropriate intervals after the oxygen had nearly disappeared in order to determine the normal conversion of styrene into polystyrene. Each sample was shortstopped with 2.0 ml. of a 0.1% water solution of hydroquinone, and the per cent. conversion of the styrene determined by weighing the residue after drying in an 80° oven for twelve to eighteen hours.

Results.—In Fig. 2 are reproduced some curves obtained. Curve 1 is for a recipe containing "1-X" soap and "1-X" persulfate. Curve 2 is for a recipe containing "1-X" soap and "5-X"
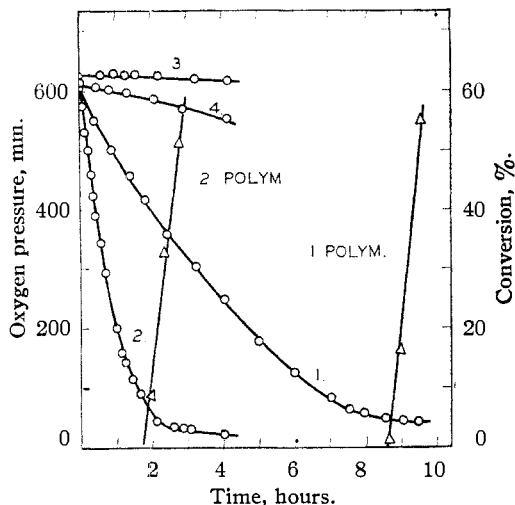
Fig. 2.—Rate of oxygen consumption, magnetically stirred system, "1-X" soap; triangles denote polymerization curves: 1, styrene–"1-X" persulfate; 2, styrene–"5-X" persulfate; 3, petroleum ether–"1-X" persulfate; 4, petroleum ether–"5-X" persulfate.

persulfate. In interpreting these curves, the initial very rapid pressure drop of 10–20 mm. has been disregarded. The effect of increasing the concentration of persulfate on the rate of oxygen uptake is clear. From curves 1 and 2 it is seen that the rates of oxygen consumption down to a pressure of about 400 mm. are not strictly in the ratio of 5:1 but are 400 mm. per hour and 90 mm. per hour at "5-X" and "1-X" persulfate, respectively, or about 4.45:1. It should be noted, however, that the induction periods observed in bottle polymerizations[1] deviate from the exact relationship nearly as much, although the bottle experiments were carried out at lower concentrations of persulfate.

The rates of polymerization are also represented in Fig. 2. Polymerization apparently begins while 30–40 mm. oxygen pressure still remains. In the bottles, however, it has been established[1] that polymerization does not begin until the dissolved oxygen has been reduced to a concentration of at most 7×10^{-4} mg./200 ml. charge, which is much less than that in equilibrium with a partial pressure of 30–40 mm. over the emulsion. This suggested that the agitation obtained with the magnetic stirring device was inadequate.

The experiments represented by curves 3 and 4 in Fig. 2 were carried out with the same recipes as those in curves 1 and 2, respectively, except that the styrene was replaced by an equal volume of petroleum ether (b. p. 100–150°). It will be observed that in the presence of this inert hydrocarbon, the uptake of oxygen is very slow, but still shows a proportionality to the concentration of persulfate. This absorption of oxygen is due to peroxidation of the soap.

In Fig. 3, curve 1 represents the uptake of oxygen by a recipe containing "1-X" sodium lino-
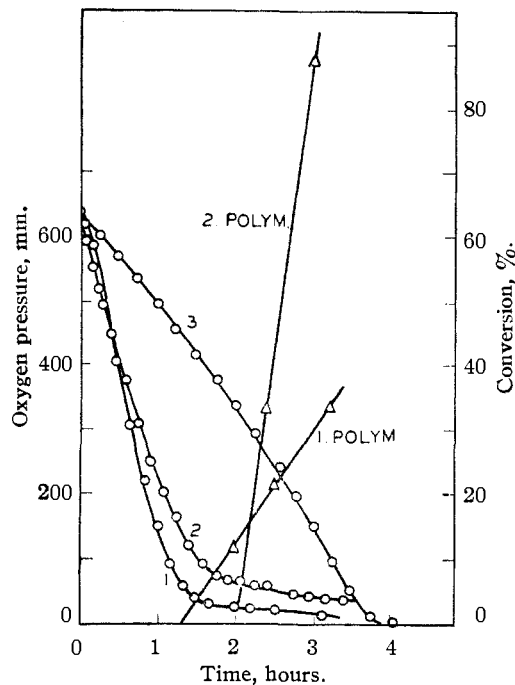

Fig. 3.—Effect of emulsifiers on the rate of oxygen consumption, magnetically stirred system, "5-X" persulfate, triangles denote polymerization curves: 1, "1-X" sodium linoleate; 2, "1-X" soap flakes; 3, no emulsifier.

leate instead of the soap flakes employed in the other runs. Curve 2 is for "1-X" soap flakes, the same as curve 2, Fig. 2. The recipes both contained "1-X" catalyst. Sodium linoleate has good emulsifying properties, but a comparison of the conversion curves observed after the disappearance of the oxygen shows that it acts as a retarder, giving a rate of polymerization only about 20% of that obtained with the commercial soap flakes. Despite its retarding effect on the polymerization, however, it has no retarding effect on the rate of oxygen uptake, and in fact appears to give a slightly faster rate than the normal soap. This appears to confirm the hypothesis that the formation of activated styrene molecules takes place in the true water phase. The slightly faster uptake of oxygen with linoleate as compared to S. F. flakes is undoubtedly due to the faster rate of peroxidation of the linoleate.

Curve 3, Fig. 3, shows the rate of oxygen uptake by a "5-X"-persulfate, soap-free recipe. The rate is evidently somewhat less in the absence of an emulsifier. The curve corresponds to that of an autocatalytic reaction, i. e., the slope of the curve appears to increase as the reaction proceeds.

It will be observed that in general the oxygen uptake curves obtained in this apparatus have a non-linear form, indicating that the expected zero order relationship

$$- dP_{O_2}/dt = KP_{O_2}^n$$

where $n = 0$, is not obeyed, but rather that n has

values of approximately 0.5. It was believed that this non-linear form could be attributed to the fact that, because of inefficient stirring, the gas phase was not at all times in equilibrium with the liquid phase. At low oxygen pressures, the rate of solution of oxygen in the emulsion became the rate-determining step in the rate of oxygen consumption. Therefore, a reaction vessel with more efficient stirring was built, in which the oxygen might dissolve in the emulsion at least as rapidly as it reacted with the activated styrene molecules.

B. Experiments Carried out with More Efficient Stirring

Accordingly, a device (Fig. 4) was constructed in which a vessel of 160-ml. capacity could be shaken back and forth at 200–300 strokes per minute in a constant temperature bath held, as before, at 50.0 ± 0.2°. This device could be connected to a manometer or a gas buret, in the same manner as described for the earlier apparatus. The ratio of liquid to vapor volume (the vapor volume includes the tubing and the manometer) was 1.010 (145.2 ml. liquid volume) in the magnetically stirred apparatus, and was 1.054 (96.8 ml. liquid volume) in the new device. Provision was not made for sampling, and rates of polymerization were not measured.
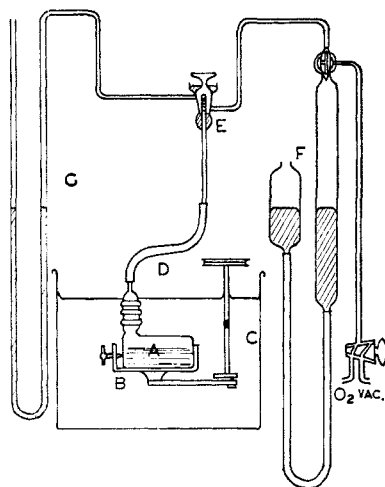

Fig. 4.—Fast-shaking reaction system for measurement of oxygen consumption: A, reaction vessel; B, clamp and shaking arm; C, oil-bath; D, rubber tubing; E, three-way mercury-sealed stopcock; F, gas buret; G, manometer.

In Fig. 5, a comparison is made of the rates of oxygen uptake at "1-X" soap with magnetic stirring (curve 1) and fast shaking (curve 2), and at "0"-soap with magnetic stirring (curve 3) and fast shaking (curve 4), "5-X" persulfate being employed in all cases. With fast shaking, the rate of oxygen uptake is independent of oxygen pressure down to 100 mm. pressure, and deviates only slightly below this pressure. With no emulsifier present, the rate of oxygen uptake is increased
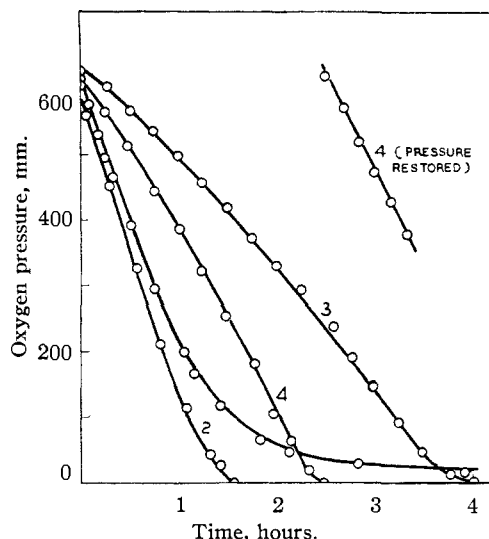

Fig. 5.—Effect of efficiency of agitation on rate of oxygen uptake, "5-X" persulfate: 1, "1-X" soap, magnetic stirring; 2, "1-X" soap, fast shaking; 3, no emulsifier, magnetic stirring; 4, no emulsifier, fast shaking.

by the more efficient agitation, as compared to the magnetic stirring, and the curve still shows the same increasing slope. However, when the reaction was prolonged by restoring the oxygen pressure after it had reached a very low value, it was found that the subsequent rate of oxygen uptake was strictly linear. The slope of the curve does not, therefore, increase indefinitely, but reaches a constant rate nearly equal to that observed in the presence of "1-X" soap.

Effect of Concentration of Potassium Persulfate and Soap.—In Fig. 6 are shown curves representing the rate of oxygen disappearance in
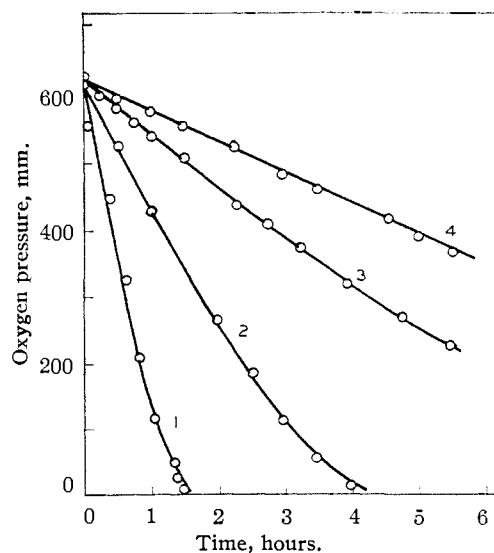

Fig. 6.—Effect of potassium persulfate concentration on rate of oxygen uptake, "1-X" soap: 1, "5-X" persulfate; 2, "2-X"; 3, "1-X"; 4, "1/2-X."

recipes containg 5, 2, 1 and $1/2$-X persulfate with "1-X" soap. In Table I, the rates of disappearance in mm./hour are summarized. These rates were measured over the linear portions of the curves, since the curves still deviate somewhat from linearity at lower oxygen pressures, despite the more efficient agitation.

TABLE I

EFFECT OF CONCN. OF $K_2S_2O_8$ ON RATE OF OXYGEN DISAPPEARANCE IN "1-X" SOAP RECIPE DURING OXYGEN INDUCTION PERIOD IN EMULSION POLYMERIZATION OF STYRENE AT 50°

Concn. $K_2S_2O_8$	Rate of O_2 reaction, mm. O_2 pressure/hour	Rate of O_2 reaction/concn. $K_2S_2O_8$
5	476	9.5
2	175	8.8
1	80	8.0
0.5	44	8.8

Table I shows that the rate of oxygen disappearance is directly proportional to the concentration of persulfate employed.

In Fig. 7 are shown curves for recipes containing 1, $1/2$, $1/4$ and O-X soap at a concentration of "5-X" persulfate. In Table II the rate of oxygen uptake of the soap-free recipe is the steady rate observed after the initial increasing rate, discussed in the preceding section. The rates for the other recipes are measured in the same way as for Table I.

TABLE II

EFFECT OF CONCN. OF SOAP ON RATE OF OXYGEN DISAPPEARANCE IN "5-X" PERSULFATE RECIPE DURING OXYGEN INDUCTION PERIOD IN EMULSION POLYMERIZATION OF STYRENE AT 50°

Concn. of soap	Rate of O_2 reaction mm. O_2 pressure/hour
1	470
0.5	400
0.25	340
0	300

Although the effect of the soap concentration on the rate of oxygen uptake is somewhat greater than that inferred from the measurement of induction periods in bottle polymerization,[1] it is still relatively small. The earlier conclusion that the formation of activated styrene molecules occurs largely in the true water phase, rather than in the soap micelles, appears justified.

Nature of the Products Formed during the Induction Period.—Having established that the rate of oxygen uptake during the induction period caused by oxygen in the emulsion polymerization of styrene at 50° is proportional to the concentration of persulfate in the water layer, and independent of the soap concentration to a first approximation, and that it is essentially zero order with respect to the oxygen pressure, it appeared desirable to identify the reaction products formed during the induction period, and to establish the mechanism of their formation.
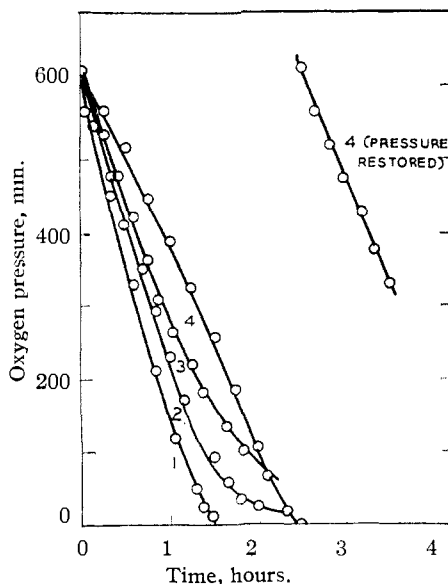

Fig. 7.—Effect of soap concentration on the rate of oxygen uptake, using "5-X" persulfate: 1, "1-X" soap; 2, "$1/2$-X"; 3, "$1/4$-X"; 4, zero soap.

It has been observed that during the oxygen induction period, there is formed a very small quantity of an alcohol-insoluble substance. This substance appears as a turbidity in the water layer when no emulsifier is employed, and its presence can be detected in recipes containing emulsifier by the appearance of a turbidity when a small quantity of the emulsion is poured into ethanol or methanol.

To learn more about this substance, experiments were carried out using four 250-ml. bottles, rotated end-over-end and in a water-bath held at 50°. These bottles were sealed with pierced metal caps and self-sealing rubber inserts, in the manner described previously.[1]

The following recipe was employed:

Styrene: 10 parts, 7.50 g.
Water: 180 parts, 135 ml.
Soap Flakes: 5 parts, 3.75 g. ("1-X")
Potassium Persulfate: 0.633 parts, 0.475 g. ("2.16-X")

Oxygen was added five times over a period of six hours to each bottle by means of a 50-ml. hypodermic syringe. The initial and final pressure in the bottles was one atmosphere. Over the six-hour reaction period, 250 ml. of oxygen, or 318 mg., was injected into each bottle. The latex obtained was coagulated with methanol giving a coagulum consisting of very fine particles. A total solids determination on the latex indicated a conversion of 57.6% (or 5.76% if the full amount of styrene had been employed), corresponding to the formation of a total of 17 g. of polymer in the four bottles. This should be compared to the normal reaction rate of this recipe in the absence of oxygen, which is about 90% conversion per hour, instead of only about 0.96% conversion per hour in the presence of oxygen. The polymer formed

resembled normal polystyrene. It burned quietly when heated on a spatula over a free flame and had an intrinsic viscosity (measured in benzene at 30°) of 2.43. This polymer appeared to be formed by a retarded normal polymerization process which occurred as a result of inefficient agitation, despite the presence of oxygen.

Another experiment was therefore carried out with the same recipe, but employing the fast-shaking reaction vessel described above. The vessel was connected to a gas buret of 250-ml. capacity, and the entire system filled with oxygen. Reaction was allowed to proceed for six hours, the pressure being maintained at 1 atmosphere. Two-hundred fifty-six mg. of oxygen was absorbed, and since the charge volume was only $^2/_3$ that employed in each of the bottles employed above, the uptake of oxygen was 21% more efficient than in the bottle experiment. Upon addition of the emulsion to twice its volume of methanol, a small quantity (90 mg.) of an alcohol insoluble substance was isolated. This substance was clearly not normal polystyrene, for it exploded when heated on a spatula over a low flame, and it melted at 90–120°, with evolution of gas.

The experiment was repeated for longer intervals of time both with and without emulsifier present, using 20 parts of styrene with emulsifier and 10 parts in the experiment without emulsifier. The concentration of persulfate was "2-X" (0.6 part per 180 parts water) in each case. The rates of oxygen uptake at a constant oxygen pressure are shown in Fig. 8, curve 2 being for the run with soap, and curve 1 for the run without soap.
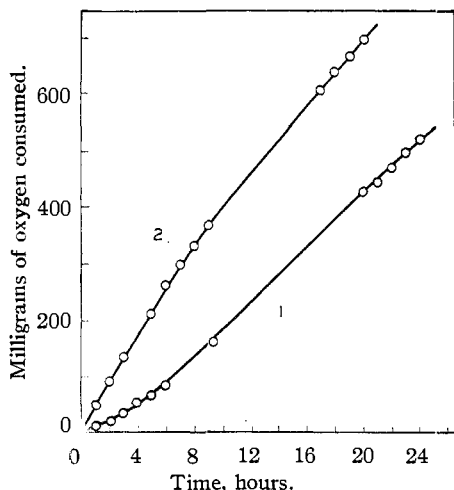

Fig. 8.—Consumption of oxygen at about 1 atm. pressure during preparation of polymeric styrene peroxide, "2-X" persulfate: 1, no emulsifier; 2, "1-X" soap.

In addition to the polymer discussed above, other reaction products may be expected. It has been found by Medvedev and Zeitlin[2] that benzaldehyde and formaldehyde are the sole products

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

of the reaction of oxygen with styrene in bulk at 80°. In the present investigation, the determination of benzaldehyde was carried out by a polarographic method explained more fully in the section on analytical procedures. No polarographically reducible substances other than benzaldehyde were found to be present. Formaldehyde was determined by a colorimetric method, also described in the analytical section.

In Table III are summarized the experimental data obtained during these two runs. The polymer obtained by methanol precipitation was exceedingly difficult to isolate quantitatively because it was very sticky and soft. The turbid mixture of emulsion and methanol was centrifuged after the removal of the bulk of the polymer, in order to improve the yield as much as possible.

TABLE III

FORMATION OF POLYMER AND ALDEHYDES DURING THE OXYGEN INDUCTION PERIOD IN THE EMULSION POLYMERIZATION OF STYRENE AT 50°, "2-X"-$K_2S_2O_8$

	Run 1	Run 2
Emulsifier	None	Soap flakes, "1-X"
Mg. polymer found	1490	2220
Hours run	24	20
Mg. O_2 consumed	520	700
Mg. HCHO formed	Very small	27
Mg. C_6H_5CHO formed	214	410
Mg. O_2 acct. for	374	578
% O_2 acct. for	72.0	82.5

The derivation of the figures for oxygen balance in Table 3 is explained in the next section. It should be noted from the above data that the rate of polymer formation in the presence of oxygen under conditions of good agitation appears to correspond to a rate of conversion of the styrene of approximately 0.111 g./hour in the "2-X" persulfate recipe, compared to a normal rate of polymerization in the absence of oxygen of about 91.0 g./hour. This represents a retardation to 0.12% of the normal rate.

Properties of the Polymer Formed during the Oxygen Induction Period.—It was found by Staudinger[3] that unsymmetrical diphenylethylene, which may be regarded as α-phenylstyrene, forms a polymeric peroxide by reaction with oxygen in the presence of light. On heating, this substance decomposes into formaldehyde and benzophenone

$$\left[\begin{array}{c} C_6H_5 \\ | \\ -C-CH_2-OO- \\ | \\ C_6H_5 \end{array}\right]_n \longrightarrow n(C_6H_5)_2CO + nHCHO$$
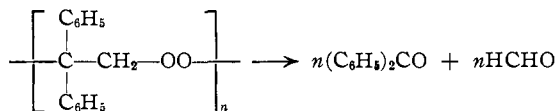
This polymer responded to none of the usual tests for peroxides, but catalyzed vinyl polymerization. Staudinger also prepared polystyrenes containing some oxygen,[4] but was unable to prepare a 1:1 compound analogous to that obtainable from

(3) H. Staudinger, *Ber.*, **58**, 1075 (1925).
(4) H. Staudinger, *Ann.*, **488**, 1 (1931).

unsym.-diphenylethylene, due to the greater tendency of styrene to enter the chain. This work was carried out in bulk, rather than in emulsion.

Farmer[5] reports that on heating α-terpinene with oxygen, a polymeric peroxide is formed, rather than the expected ascaridole
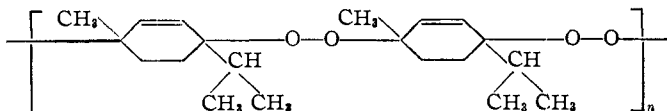
This substance decomposes explosively when heated above 130°.

Isolation of a pure 1:1 styrene–oxygen copolymer, or polymeric styrene peroxide, has not been hitherto reported, but the properties of the polymer obtained in runs 1 and 2 (Fig. 8) suggested that it might be such a compound
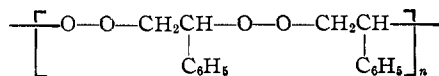
Elementary analysis[5a] of the polymer corresponds reasonably well with that calculated for the above structure:

Anal. Calcd. for $C_8H_8O_2$: C, 70.50; H, 5.86; O, 23.60. Found: Run 1, C, 71.05; H, 6.04; O (diff.), 22.9; Run 2, C, 71.13; H, 6.27; O (diff.), 22.6.

The percentages of oxygen thus found, together with the oxygen appearing as benzaldehyde and formaldehyde, were used in calculating the "oxygen accounted for" in Table III; most of the oxygen consumed is found in this polymer.

The polymer exploded on heating rapidly above 100°. In order to determine the products of thermal decomposition, which were expected to be largely benzaldehyde and formaldehyde by analogy to the behavior of *unsym.*-diphenylethylene peroxide, small quantities of the polymers were decomposed in sealed glass ampules, and the products analyzed for these aldehydes in the manner detailed in the section on "Analytical Procedures," From the decomposition of the Run 2 polymer (soap present), about 60% of the expected quantity of benzaldehyde was found, and from the Run 1 polymer (no soap present) about 80%. Formaldehyde was present in the decomposition products, but was not found in the same molar quantity as benzaldehyde. The decomposition to aldehydes is evidently not quantitative, since considerable gas is evolved.

The polymer was found to catalyze the bulk polymerization of styrene. One-tenth of a gram of the polymer was dissolved in about 2 ml. of freshly distilled styrene, and the mixture heated in a small test-tube for four hours at 80°. At the end of this time, the styrene had polymerized to a solid mass, whereas a control sample containing no peroxide

polymer only increased somewhat in viscosity under the same conditions.

Confirmation of the peroxide nature of the polymer was also obtained from a study of its reduction at the dropping mercury electrode. The solvent employed contained (by volume) 58% benzene, 37% ethanol and 5% water. The final solution was 0.05 M in ammonium acetate as supporting electrolyte. Solutions were flushed free of oxygen. Waves were obtained at concentrations of 0.000775 and 0.001550 molar, calculated per

—CHCH₂—OO— unit, and are shown in Fig. 9 (curves 2 and 3, respectively). These waves resemble those found by Stern and Polak[6] for diethyl peroxide in 0.01 N hydrochloric acid, 0.01 N sodium hydroxide and 0.1 N lithium chloride. Diethyl peroxide, however, did not show a drop in the diffusion current at potentials more negative than −1.5 volts as was found with the peroxide polymer.
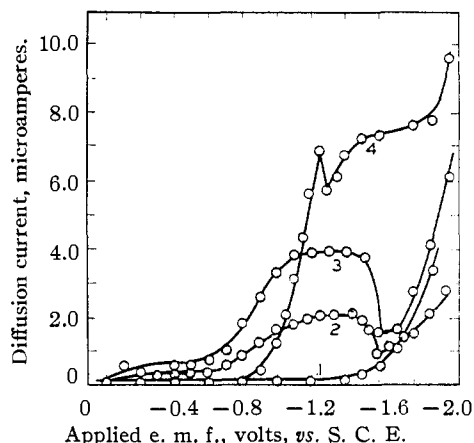

Fig. 9.—Polarographic reduction waves of polymeric styrene peroxide and *t*-butyl hydroperoxide; solvent, 58% benzene, 37% ethanol, 5% water (by vol.); 0.05 M in ammonium acetate: 1, blank; 2, polymer: 0.000775 M in monomer units; 3, polymer: 0.001550 M in monomer units; 4, *t*-butyl hydroperoxide: 0.00109 M.

In order to afford a comparison with a known substance, the polarogram of *t*-butyl hydroperoxide was determined in the same solvent. Curve 4 is the reduction wave of this substance at a concentration of 0.00109 M. This peroxide gives a small maximum of an abnormal type and its reduction occurs close to −1.0 volt, which is more negative than that of reduction of the polymer peroxide. The diffusion current data for these two substances can be summarized as follows, the concentration of polymer being expressed in moles of monomer units per liter.

Polymer: $\dfrac{i_d \text{ (at } -1.4 \text{ volt)}}{\text{conc. (moles/l.)}} = 0.239 \times 10^4$ average (1)

(5) E. H. Farmer, *Trans. Faraday Soc.*, **21**, 122 (1946).

(5a) Performed by C. W. Beazley, Microtech Laboratories, Skokie, Ill.

(6) V. Stern and S. Polak, *Acta. Physicochim., U. R. S. S.*, **11**, 797 (1939).

t-Butyl hydroperoxide: $\dfrac{i_d \text{ (at } -1.75 \text{ volt)}}{\text{conc. (moles/l.)}}$ =

$$0.605 \times 10^4 \text{ average} \quad (2)$$

It is interesting to note in the case of the polymer peroxide that after a certain voltage region of constant diffusion current, the latter suddenly drops to low values (curves 1 and 2) just before the large wave due to reduction of the supporting electrolyte starts. This drop indicates that the polymer peroxide must be adsorbed on the surface of the mercury in the region of constant diffusion current and that it is desorbed at a potential more negative than −1.5 v. Such dependence of adsorption and desorption upon the potential of mercury is found with several organic compounds.

The relatively large value of the diffusion current constant (i_d/c) indicates that the polymer peroxide must be adsorbed in its full length on the surface of the dropping mercury. It must be remembered that under otherwise identical conditions the diffusion current constants of two substances are in the ratio of the square roots of their diffusion coefficients. The difference between the diffusion currents per mole of monomer unit for the polymer on one hand and for the lower molecular weight peroxide on the other, must be attributed to the large difference in molecular weight.

The intrinsic viscosity of the polymer was determined. The polymer was dissolved in toluene, precipitated with a large volume of methanol, vacuum dried at room temperature for twenty-four hours, then redissolved in toluene. The relative viscosity at 25° of this 1.442% solution was measured in an Ostwald pipet and found to be 1.09. The intrinsic viscosity, calculated from the expression

$$\eta_i = \frac{2.303 \log \eta_{\text{rel.}}}{\text{conc., g./100 ml. solvent}}$$

was found to be 0.060. Using unpublished data of Ewart, Roe, Tingey and Wales[7] for a series of fractions of modified polystyrene, it is estimated from this viscosity measurement that the number average molecular weight is probably of the order of 5000. This figure admittedly is only an approximation, because the results of Ewart, *et al.*, referred to polystyrene and not to polystyrene peroxide, because an extrapolation of their results to a viscosity somewhat lower than that of any of their fractions had to be made, and because our material is probably not so homogeneous with respect to molecular weight as were their fractions.

A direct test of the peroxide nature of the polymer was made by the iodimetric method employing acetic anhydride as a solvent as recommended by Nozaki.[8] The maximum value found for peroxide oxygen was 14.1%, which is considerably lower than the theoretical value of about 22.5%. Elementary analysis was not performed upon the

(7) R. Ewart, C. Roe, H. Tingey and M. Wales, private communication.

(8) K. Nozaki. *Ind. Eng. Chem.*, **18**, 583 (1946).

sample of polymer used in this test, but the polymer was prepared in a manner identical to that reported as Run 1 (no emulsifier). The value 14.1% was attained only after standing twenty hours at room temperature. Higher results were not obtained by subsequent heating at 100° for fifteen minutes.

Further Experiments on the Nature of the Reaction of Styrene with Oxygen during the Induction Period.—(1). From Curve 3, Fig. 6, for the rate of reaction of oxygen with a "1-X" soap, "1-X" persulfate recipe, it can be calculated that the rate of oxygen disappearance is about 0.0085 mole/hour/liter of aqueous phase. From polarographic measurements, which are not reported fully at this time, of the rate of disappearance of persulfate under these conditions, it appears that 80–100 moles of oxygen react for every mole of persulfate reacting. The first step of the mechanism postulated at the beginning of this paper is

$$K_2S_2O_8 + M \longrightarrow M^* \text{ (activated styrene molecule)} \quad (1)$$
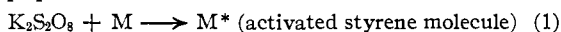
The persulfate ions, whether they react directly with the styrene molecules or produce hydroxyl free radicals which in turn activate the styrene molecules, give rise from stoichiometric considerations to one or at least to no more than two activated styrene molecules (free radicals) for each persulfate ion disappearing. These facts suggest, therefore, that, in the formation of polymer peroxide, one activated styrene molecule formed by persulfate results in the over-all reaction of 40 to 100 molecules of oxygen and of styrene.

(2) It is of interest to compare the rate of oxygen uptake during the induction period with the rate of normal emulsion polymerization of styrene in the absence of oxygen. In the following considerations, we assume that during the induction period, every free radical formed reacts with oxygen, and that during normal polymerization every free radical initiates a polymer chain. If the rate of oxygen disappearance during the induction period were equal to the rate of formation of styrene free radicals during normal polymerization, we might calculate the number average molecular weight $(\overline{M}_n)$ of the polymer formed during normal polymerization.

Adopting the classical view that one polymer molecule results from the reaction of two styrene free radicals, one for initiation and one for termination, we find for a "1-X" soap, "1-X" persulfate recipe

$$\overline{M}_n = \frac{\text{rate of chain propagation}}{\text{rate of chain initiation}}$$

$$= \frac{\text{rate of polymerization (g./hour/liter of aqueous phase)}}{0.5 \text{ rate of O}_2 \text{ uptake (moles/hour/liter of aqueous phase)}}$$

$$= \frac{470}{.00425} = 110,000$$

The intrinsic viscosity of polystyrene at about 30% conversion (the intrinsic viscosity is found nearly independent of conversion), prepared in

the above recipe, is 14.50, measured in benzene at 30°. By extrapolating the data of Ewart, Roe, Tingey and Wales[7] it is possible to estimate that the polymer obtained using 1-soap ($\eta_i = 14.50$) has a weight-average molecular weight in the neighborhood of 5,000,000. Since the number-average molecular weight of polystyrene has been found in many cases to be about one-half the weight-average, it may be estimated that the number-average molecular weight is about 2,500,-000. These are, of course, very rough estimates, but it is certain that the molecular weight is very high, possibly 20–25 times the value 110,000 calculated above. This suggests that one styrene free radical produced by persulfate does not react with but one oxygen molecule, but rather that many oxygen molecules, of the order of 25, react in a chain process initiated by a single styrene free radical. Further consideration of this chain process is given in the "Discussion."

Although the rate of activation is *proportional* to the rate of oxygen consumption, it is evident, from the present argument, that the rate of activation cannot be *equal* to the rate of oxygen consumption, but must be of the order of 25 times smaller.

(3) Data have been obtained on the effect of *p*-benzoquinone in the emulsion polymerization of styrene, and will be more fully reported at a later date. In connection with the present study, it can be stated that this substance appears to be many times more effective than an equal molar quantity of oxygen in preventing emulsion polymerization of styrene. In working with quinone, however, it was found necessary to use dodecyl-amine hydrochloride as emulsifier (*p*H about 5.6), since the quinone is rapidly destroyed at the *p*H of the fatty acid soap recipe (*p*H about 9.5), and therefore its effect in the fatty acid soap recipe cannot be observed. Comparison of its effect with the inhibitory effect of oxygen is somewhat obscured, therefore, but it appears that quinone is 20–30 times more effective.

From evidence obtained in this laboratory and by others, *e. g.*, Kern and Feuerstein,[9] it appears that each quinone molecule reacts with only two styrene free radicals. Its greater effectiveness as compared to oxygen seems to be due to the fact that it does not permit the propagation of a chain reaction, whereas 20–30 molecules of oxygen (and of styrene) react for each styrene free radical produced during the oxygen induction period.

Analytical Procedures.—Benzaldehyde in reaction mixtures was determined polarographically. In general, 2.5 ml. of the reaction mixture and 2.5 ml. of 1 *M* ammonium acetate were pipetted into a 25-ml. volumetric flask, diluted to volume with absolute alcohol, and flushed free of oxygen in the polarographic cell with purified nitrogen. The reduction wave of benzaldehyde was plotted manually, and the diffusion current at −1.7 volts (*versus* standard calomel electrode) was measured and compared to a previously prepared calibration curve. Formaldehyde does not interfere.
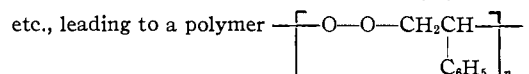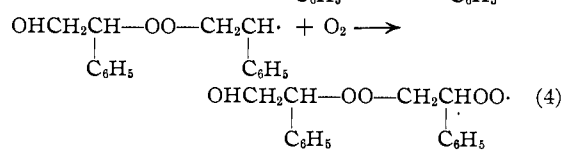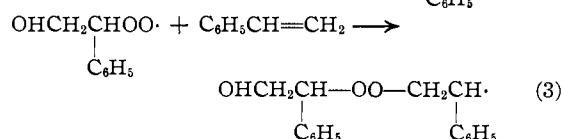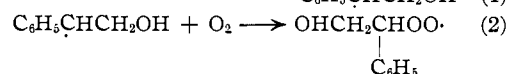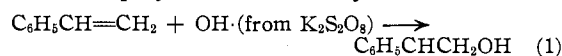
(9) W. Kern and K. Feuerstein. *J. prakt. Chem.*, [2] **158**, 186 (1941).

Formaldehyde was determined by the method of Bricker and Johnson,[10] which makes use of the formation of a colored complex when formaldehyde is heated with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) in concentrated sulfuric acid. There is reason to believe that this method gives low results when applied to samples of the reaction mixtures used in this work.

To study the thermal decomposition products of the polymeric styrene peroxide, small quantities of the polymer were sealed into glass ampules and heated to 180° over a period of two hours. The ampule was then broken under ethanol cooled to −20°, and its contents dissolved. The above methods for the determination of benzaldehyde and formaldehyde were then applied to this ethanol solution. Twenty-eight milligrams of the polymer from Run 1 gave 17.6 mg. of benzaldehyde and 1.4 mg. of formaldehyde. Thirty milligrams of the polymer from Run 2 gave 14 mg. of benzaldehyde and 0.7 mg. of formaldehyde.

Discussion

The experimental results suggest the following chain mechanism for the reaction of oxygen during the induction period produced by oxygen in the emulsion polymerization of styrene

$$C_6H_5CH{=}CH_2 + OH\cdot(\text{from } K_2S_2O_8) \longrightarrow$$
$$C_6H_5\dot{C}HCH_2OH \quad (1)$$

$$C_6H_5\dot{C}HCH_2OH + O_2 \longrightarrow OHCH_2CHOO\cdot \quad (2)$$
$$\underset{C_6H_5}{|}$$

$$OHCH_2CHOO\cdot + C_6H_5CH{=}CH_2 \longrightarrow$$
$$\underset{C_6H_5}{|}$$

$$OHCH_2CH{-}OO{-}CH_2CH\cdot \quad (3)$$
$$\underset{C_6H_5}{|}\qquad\underset{C_6H_5}{|}$$

$$OHCH_2CH{-}OO{-}CH_2CH\cdot + O_2 \longrightarrow$$
$$\underset{C_6H_5}{|}\qquad\underset{C_6H_5}{|}$$

$$OHCH_2CH{-}OO{-}CH_2CHOO\cdot \quad (4)$$
$$\underset{C_6H_5}{|}\qquad\underset{C_6H_5}{|}$$

etc., leading to a polymer $\left[{-}O{-}O{-}CH_2\underset{\underset{C_6H_5}{|}}{CH}{-}\right]_n$

The benzaldehyde and formaldehyde may arise from thermal decomposition of the polymer, or by a side reaction of the peroxide free radicals.

The exact nature of the activation step (1) is unknown, although it is certain that styrene and persulfate interact to form styrene free radicals. For convenience, we have formulated this as the reaction of hydroxyl free radicals, produced by the persulfate, with the styrene. Such a mechanism has been suggested by Baxendale, Evans and Park[11] for the polymerization of acrylonitrile in water solution, initiated by hydrogen peroxide and ferrous ion. For the present purpose, however, it is immaterial whether this formulation is correct, or whether the activation proceeds by direct attack of persulfate ion upon styrene, or by some other means.

It is of some interest next to consider briefly the locus of the activation reaction. In 1938,

(10) C. Bricker and H. Johnson. *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 400 (1945).

(11) J. Baxendale. M. Evans and G. Park. *Trans. Faraday Soc.*, **42**, 155 (1946).

Fikentscher[12] postulated that in emulsion polymerization, the polymerization reaction occurs in the aqueous phase. This was substantiated by Fryling and Harrington,[13] who postulated that solubilization of monomer in soap micelles played an important role in the polymerization. Harkins and co-workers[14] presented evidence that micelles are the main loci of the polymerization for the period of conversion during which the soap is not yet adsorbed on the polymer particles.

Although there is little doubt that the propagation of the chain actually occurs in the soap micelles, the fact that the rate of oxygen uptake during the induction period is only slightly dependent on the concentration of soap provides strong evidence that the activation reaction occurs mainly or entirely in the "true" water phase, rather than in the soap micelles. (On the other hand, the rate of polymerization of styrene has been found in this Laboratory to be proportional to the square root of the soap concentration when S. F. flakes soap is used as emulsifier.) The activation step may well be strictly independent of the soap concentration, and the subsequent steps may to some extent take place in the micelle, thus giving rise to the small degree of dependence of the rate of oxygen consumption on soap concentration observed.

The reaction of oxygen with styrene free radicals (Step 2) is probably very rapid, and occurs to the exclusion of the attack of this radical on another styrene molecule, provided that oxygen is efficiently supplied to the emulsion. This is indicated by the fact that normal polymerization is entirely suppressed by oxygen under conditions of efficient agitation. The reaction of the peroxide radical with a styrene molecule (Step 3) is evidently much slower than the reaction of a styrene free radical with a styrene molecule, because the over-all rate of formation of the peroxide polymer is only about 0.1% as large as the rate of normal polymerization. Reaction (3) is considerably faster, nevertheless, than reaction (1), which is the rate-determining step.

The reaction of oxygen with the peroxide free radical is not formulated as a possible step in this mechanism, because it would lead to such improbable structures as

$$\text{OHCH}_2\text{CHOO--OO·}$$
$$|$$
$$\text{C}_6\text{H}_5$$
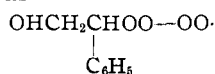
It appears that the peroxide radical can react only with another styrene molecule, although the radical resulting from this union (Step (3)) may react with either oxygen or another styrene molecule. Thus, depending on the efficiency with which oxygen is supplied, copolymers of all compositions, containing from 23.5% oxygen (corresponding to the polymer shown in Step (4)), to no oxygen, may

be formed. The polymer actually isolated can be regarded as a 1:1 copolymer of oxygen and styrene. Moreover, it appears from the above consideration that it must be an ideal copolymer, with the monomer units in strict alternation.

The value of n appears from the molecular weight of polymer formed to be about 40. This is in approximate agreement with the values deduced from the experiments mentioned in the preceding section.

The mechanism by which the radicals are terminated is not known. From our experimental results it can be concluded that the termination reaction cannot be represented as the reaction of two styrene peroxide chain radicals with each other, whereas in the normal polymerization the termination occurs by interaction of two free radicals. If such a reaction occurred in the termination of styrene peroxide chain free radicals, the rate of oxygen uptake would be proportional to the square root of the persulfate concentration, whereas we have found it to be directly proportional.

George and Robertson[15] have found that in the thermal oxidation of tetralin by oxygen the observed kinetics cannot be explained by assuming any of the following recombination steps

$$\text{R·} + \text{R·}$$
$$\text{R·} + \text{RO}_2·$$
$$\text{RO}_2· + \text{RO}_2·$$
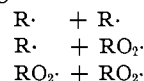
They conclude that if the free radical mechanism is to be retained, some unimolecular termination step must be postulated. From a study of this reaction in the presence of inhibitors, they further conclude that the chain carriers are not free radicals, but energy-rich molecules, which can dispose of their excess energy by unimolecular termination reactions. However, since previous studies[16] have shown that the kinetics of the normal emulsion polymerization of styrene in the absence of oxygen is consistent with a free radical mechanism, it does not appear probable at present that the chain carriers are of an entirely different nature when oxygen is present.

Summary

By direct measurement of the rate of oxygen consumption during the induction period caused by oxygen in the emulsion polymerization of styrene at 50°, it has been found that the reaction of oxygen during the induction period is essentially zero order with respect to oxygen pressure, nearly independent of the concentration of emulsifier, and directly proportional to the concentration of persulfate.

The oxygen consumed during the induction period has been largely accounted for. It reacts mainly to form a polymeric styrene peroxide, and to a minor extent to produce benzaldehyde and formaldehyde. A polymer has been isolated which

(12) H. Fikentscher, Angew. Chem., 51, 433 (1938).

(13) C. F. Fryling and E. W. Harrington, Ind. Eng. Chem., 36, 114 (1944).

(14) W. D. Harkins, J. Chem. Phys., 13, 381 (1938).

(15) P. George and A. Robertson, Proc. Roy. Soc. (London), 185, 309 (1946).

(16) I. M. Kolthoff and W. J. Dale, THIS JOURNAL, 67, 1672 (1945).

has a composition corresponding to a 1:1 copolymer of oxygen and styrene. This copolymer contains of the order of 40 styrene peroxide units.

A chain mechanism has been proposed to account for the observed kinetics and products of the reaction of styrene with oxygen during the oxygen induction period. The rate of copolymerization of styrene with oxygen is of the order of a thousandth smaller than the normal rate of emulsion polymerization of styrene in a recipe containing the standard amount of soap.

Photochemical Studies. XXXVIII. A Further Study of the Photochemistry of Methyl *n*-Butyl Ketone

BY WALLACE DAVIS, JR.,[1] AND W. ALBERT NOYES, JR.

The photochemical decomposition of methyl *n*-butyl ketone was first studied by Norrish and his co-workers,[2] who showed that there are two reactions, one to give acetone and propylene, the other to give carbon monoxide and a series of other compounds, mostly hydrocarbons. Bamford and Norrish concluded that the reaction giving acetone and propylene proceeds without intermediate free radicals whereas the second does involve free radicals. It has been shown, however, that the acetone–propylene reaction might be explained by a series of free radical reactions.[3] The ratio of acetone to propylene was about 3:4,[4] but was not very precisely determined.

The evidence for or against free radicals in the production of acetone and propylene in the gas phase reaction was based mainly on the invariance of quantum yield with varying conditions. The reaction in paraffin solution performed by Bamford and Norrish also indicated that no unsaturation accompanied this reaction other than that due to the propylene itself, and this further supported the idea that free radicals are not involved. The evidence, while reasonably good, was not conclusive, and the work described in the present paper was designed to answer several important questions.

Experimental

A General Electric Company Type AH-6 high-pressure mercury arc, red purple corex glass, and filter solutions of nickel chloride, potassium acid phthalate, and potassium chromate[5] were used to give approximately monochromatic radiation of wave lengths 3130 Å. This arc operates at such a high pressure that the emission lines are exceedingly broad. A slight change in operating conditions may produce an appreciable change in the wave length–intensity distribution of this arc-filter combination. Since the absorption coefficient of methyl *n*-butyl ketone (and, in general, of all other ketones) is changing quite rapidly with wave length near 3130 Å., it is evident that measurements with this type of light source do not correspond to monochromatic light and might not be very reproducible. However, surprisingly good constancy was found for the "integrated" absorption coefficient in these experiments. The absorption should be obtained in each individual experiment.

The absolute values of the quantum yield are referred to acetone vapor at 120° as a primary standard. The quantum yield of carbon monoxide formation from acetone at that temperature is unity.[6] Since the acetone and methyl *n*-butyl ketone were used in the same cell with the same light source, all corrections for window reflection would be negligible providing the percentage absorptions in the two cases were identical. In general, however, the acetone pressure was higher and corrections for window reflection were necessary, although small.

The corrections for transmission and absorption by windows were applied as follows:[7]

Let α be the fraction of light absorbed by a single window with a single passage of light, and let it be assumed that the two windows of the cell are identical. Let F = fraction of light reflected at a gas–quartz interface and β = the fraction of light absorbed by the gas during a single passage of light. After multiple reflections it can be shown that the fraction of the incident light reflected by one window is

$$R = F\left[1 + \frac{(1 - F)^2(1 - \alpha)^2}{1 - (1 - \alpha)^2 F^2}\right] \tag{1}$$

The fraction of incident light absorbed by one window is

$$A = \frac{(1 - F)\alpha}{1 - (1 - \alpha)F} \tag{2}$$

(1) National Research Council Predoctoral Fellow, 1945–1946. Part of the work described in this article was performed under Contract N6onr-241, Task I with the United States Navy.

(2) R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.*, 874 (1934); C. H. Bamford and R. G. W. Norrish, *ibid.*, 1538 (1938); B. M. Bloch and R. G. W. Norrish, *ibid.*, 1638 (1935).

(3) J. E. Wilson and W. A. Noyes, Jr., THIS JOURNAL, **65**, 1547 (1943).

(4) See also W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **64**, 2376 (1942).

(5) R. E. Hunt and W. Davis, Jr., *ibid.*, **69**, 1415 (1947).

(6) D. S. Herr and W. A. Noyes, Jr., *ibid.*, **62**, 2052 (1940).

(7) For details of the derivations of the equations in the following paragraphs see R. E. Hunt and T. L. Hill, *J. Chem. Phys.*, **15**, 111 (1947).