be obtained with a slope less than unity for quantities of barium as low as 10^{-10} g. atom, and can therefore be used for analysis of barium chloride solutions containing amounts of barium down to that order of magnitude.

However, the experimental procedure involves some difficulties since it requires constant *p*H, volume and salt concentration for a whole series of samples in addition to specific techniques in chemical manipulation with the small quantities of adsorbent and adsorbate indicated. It necessitates that all Geiger counter measurements be carried out over a sufficient interval of time to obtain mean values of each individual determination from the decay curve. In this way fluctuation of background, change in sensitivity of Geiger–Mueller tubes and variations due to geometry of samples are eliminated. A single measurement of tracer for a given experiment is insufficient for the required exactness.

Some of the conditions which are desirable using the techniques described are as follows:

(a) ***p*H.**—A *p*H of not greater than 8 and preferably as low as 7.5 (or possibly even less if a corresponding increase in adsorbent were used) is favorable.

(b) **Salt.**—The ammonium chloride concentration should be kept as low as is possible considering the acidity necessary for stability of the original dilute barium, tracer and iron solutions.

(c) **Volume.**—Total final volume (after titration) of less than 10 ml. is not to be desired and a volume of around 30 ml. seems to result in increased accuracy (as compared to 10 ml.) in manipulation. This larger volume also makes possible lower salt concentrations.

(d) **Quantity of Adsorbent.**—One or 2 × 10^{-5} g. atom of iron as hydrous oxide is sufficient for 10-ml. samples and as high as 6 × 10^{-5} g. atom of iron have been used for 30-ml. samples. Quantities below 1 × 10^{-5} g. atom of iron do not settle well so cause errors in adsorbent pipetted with solution. A quantity of the order of 6 × 10^{-5} g. atom of iron (other conditions being as above) results in adsorption of 40% or more leaving only 60% or less in solution and since it is the activity of a portion of the solution which is measured, the accuracy of the measurements decreases rapidly beyond this ratio. Therefore quantities of from 1 to 6 × 10^{-5} g. atom of iron, with other conditions as described, are suggested.

COLUMBUS, OHIO RECEIVED JULY 5, 1946

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Mechanism of Emulsion Polymerizations. II. The Effect of Oxygen on the Emulsion Polymerization of Styrene[1]

BY I. M. KOLTHOFF AND W. J. DALE

Recently Barnes[1a] has interpreted the dualistic role of oxygen in the catalyst-free photo- and thermo-polymerizations, and also the catalyzed thermal polymerizations of vinyl compounds. Under such conditions an induction period is found during which the oxygen reacts with one or more constituents of the system with formation of peroxides. The peroxide acts as a "catalyst" at the end of the induction period. When the initial system contains a "catalyst" in addition to oxygen, the "catalyst" also produces free radicals which react with oxygen. Under these conditions the oxygen acts like a typical inhibitor. The extent to which it exerts a catalytic effect after the polymerization begins may be expected to depend on the ratio of the amount of "catalyst" and oxygen present in the system.

The present paper deals with the induction period caused by oxygen in the emulsion polymerization of styrene. Previously[2] it has been shown that oxygen acts like a typical inhibitor with persulfate as "catalyst." In unpublished work the authors in coöperation with D. R. May devised a method by which the disappearance of oxygen during the induction period in the emulsion polymerization of styrene could be measured with the aid of a rotating platinum micro-wire electrode. It was shown in this way that "normal" polymerization of styrene does not start until the oxygen has practically disappeared. Thus the oxygen acts like a typical inhibitor which is being used up during the induction period.

In the same study it was also shown polarographically that at the end of the induction period only traces of alcohol soluble peroxides were present, the amount of peroxides being only a minor fraction of the amount of oxygen consumed during the induction period.

In the present paper and subsequent papers we confine ourselves to a study of the various factors which affect the induction period caused by oxygen in the emulsion polymerization of styrene. The interpretation of the experiments yields interesting information in regard to the kinetics and locus of the activation of styrene molecules in emulsion polymerization.

We have shown previously[2] that with the use

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(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(1a) C. E. Barnes, THIS JOURNAL, **67**, 217 (1945).

(2) I. M. Kolthoff and W. J. Dale, *ibid.*, **67**, 1672 (1945).

of pure materials no induction period was found in the absence of oxygen in the charges. On the other hand, if the styrene or the emulsifier contains inhibitors an induction period is found even in the complete absence of oxygen. Failure to remove oxygen completely from the charges or the presence of other materials may account for observations by Vinograd,[3] Frilette[4] and Hohenstein, *et al.*,[5] that removal of oxygen cuts down the induction period but does not eliminate it.

It is of interest to mention that oxygen not only prevents the start of the polymerization when present in the original charge, but also prevents the continuation of the polymerization when it is added to a styrene latex. Air or oxygen added to such a latex stops the further conversion until all of the oxygen has been consumed. Thus, oxygen added to a latex acts like a "temporary short-stop."

Experimental

In these experiments it is essential to ensure rapid establishment of distribution equilibrium of the oxygen between the gas phase and the liquid phases. Failure to do so may cause the polymerization to start before all the oxygen has disappeared. Under such conditions an apparent retarding effect of oxygen during the early stages of polymerization is observed and the interpretation of experimental results becomes very involved.

In our work the polymerizations were carried out in 8-oz. bottles (volume 253 ml.) which had ordinary metal screw caps. In general four such bottles were charged with distilled styrene, a commercial soap, persulfate and water, making a total volume of 210 ml. The volume of the air above each charge was 43 ml. The bottles after charging were sealed (*v. i.*) and placed on a rotating drum in a 50° (±0.1°) thermostat and were rotated end over end at 35 r. p. m. Each bottle was sampled usually at 10-minute intervals as described below.

The sampling was done with the aid of hypodermic syringes. The paper inserts of the metal caps had been removed and the caps pierced with about 12 small holes. A thin ($^1/_8$") self sealing rubber insert[6] was then fitted into each cap. Sampling of a charge began immediately after termination of the induction period, which could be estimated within five minutes by the appearance of a blue tinge in the white translucent latex. At ten-minute intervals thereafter the bottle was removed from the thermostat, held steadily in an inverted position, and the cap was pierced with a 22-gage needle fitted to a 5-ml. hypodermic syringe. A trace of paraffin oil on the syringe piston and on the needle point aided the operation. About 1 to 2 ml. of the latex was withdrawn and the time was noted to the nearest minute. The bottle was replaced on the thermostat and the sampled latex ejected from the syringe into a small preweighed aluminum dish which contained 10.0 ml. (9.95 g.) of a 0.02% aqueous hydroquinone solution at room temperature. The water served to cool the latex to a point where loss by evaporation during weighing was not appreciable. The latex with the dish and water was now weighed and then placed in an 80°-oven to evaporate the water and unreacted monomer. After drying to constant weight the per cent. conversion was calculated from the weight of dry solids, the weight of latex sample, and the known concentration and weight of the charge. This is illustrated for a charge weighing a total of 203 g., and containing 71.2 g. of styrene in addition to 180 parts of water, 5 parts of soap and 0.3 part of persulfate per 100 parts of monomers

$$\%\ \text{Conversion} = \frac{(100)(\text{weight dry residue})(203)}{(\text{weight latex})(71.2)} - 5.0 - 0.3$$

The operation of sampling takes less than twenty seconds. Loss of latex by evaporation during weighing is negligible using a damped balance. The use of a thinner self sealing insert is not advised since the thinner inserts do not prevent the drawing in of air during sampling as the oxygen is used up. If the needle is not held steadily during sampling the puncture in the cap is wedged open by the deflected needle which allows air to be drawn into the bottle. It was found desirable to use a new area of the cap for each sample during a given run; the holes are ordered by a clock system.

The use of syringes for injecting materials into a latex through a self sealing cap[6] was introduced by the University of Illinois Rubber Research group[7] under the direction of Professor C. S. Marvel and was adopted for sampling of latex by Houston.[8]

We find the above method for the determination of conversion more precise and accurate and also less subject to error than the method based upon measuring the change in volume during the polymerization (*e. g.*, Fryling[9]).

In the presence of persulfate an apparent zero order rate of conversion of styrene up to 50 to 60% conversion is found. This allows extrapolation to "zero" conversion by drawing a straight line through the points corresponding to less than 60% conversion.

Reagents

Potassium Persulfate.—A C. P. product was recrystallized twice from conductivity water. The solution was not heated above 50° and the crystals after washing with cold water were dried to a constant weight in a vacuum desiccator. We have found that some apparently good commercial products of potassium persulfate contain enough nitrogen compounds or other contaminants to retard the polymerization of styrene. Solutions of persulfate in water were prepared freshly before using.

Emulsifier.—Commercial soap (S. F. flakes, Procter and Gamble Co.) which is composed of the sodium salts of stearic, palmitic and oleic acids was found satisfactory in the present work.

Water.—Conductivity water.

Styrene.—Commercial Dow styrene was used with a reputed purity of at least 99.5%. This was distilled *in vacuo* just before using at a temperature of 40°. A supply of distilled styrene may be kept frozen in the dry ice box. As shown below a careful distillation is sufficient to remove the inhibitors.

In the "standard recipe," concentrations of the constituents refer to grams per 100 g. of styrene. In these experiments, 71.2 g. of styrene was used in a charge. In addition the following constituents were present: 128.2-g. of water in which were dissolved in separate portions the soap and the persulfate (180 parts of water per 100 styrene); 31.4 ml. of a 0.680% potassium persulfate solution (0.3% $K_2S_2O_8$ based on monomer = "1" $K_2S_2O_8$); 100 ml. of a 3.56% soap solution at 50° (5.0% soap based on monomer).

Thermostat temperature in all experiments was 50°. The amount of persulfate, soap, and air in this recipe has been varied. For the sake of convenience the amount of

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(3) J. R. Vinograd, L. L. Fong and W. M. Sawyer; J. R. Vinograd and G. S. Ronay; J. R. Vinograd and W. M. Sawyer; papers presented before the Colloid Division at the A. C. S. meeting in New York, September 13, 1944.

(4) V. J. Frilette, paper presented before the Organic Division, September 14, 1944.

(5) W. P. Hohenstein, S. Siggia and H. Mark, *India Rubber World*, **111**, 173 (1944); S. Siggia, W. P. Hohenstein and H. Mark, *ibid.*, **111**, 436 (1945); W. P. Hohenstein, F. Vingiello and H. Mark, *ibid.*, **110**, 291, 1944.

(6) S. A. Harrison and E. R. Meincke, B. F. Goodrich Co., private communication.

(7) R. Frank and D. Shepherd, University of Illinois, private communication.

(8) R. J. Houston, B. F. Goodrich Co., private communication.

(9) C. F. Fryling, *Ind. Eng. Chem., Anal. Ed.*, **16**, 1 (1944).

persulfate in the "standard" recipe (0.3% referred to styrene) is designated as "1." The notation "2" persulfate refers to double the amount of persulfate that is used in the "standard" recipe, etc. The same notation is used when the amount of soap is varied.

In making a charge the hot soap solution was pipetted into the bottle and allowed to gel at room temperature; the persulfate solution was added followed by styrene.

Induction Periods in the Absence of Air. When the reagents were purified according to the above procedure we did not find an appreciable induction period in the absence of oxygen. This was shown by the following experiment. In each of two 8-oz. bottles were placed the aqueous ingredients (except the soap). A glass tube was extended to the bottom of each and purified nitrogen was bubbled through the solutions for fifteen minutes. In a separate vessel the purified nitrogen was bubbled through the distilled styrene for a period of twenty minutes. After fifteen minutes the glass tubes in the bottles were elevated above the water surface and styrene was rapidly pipetted into the bottles. The nitrogen bubbling through the upper styrene layer was continued carefully (so that the two layers would not mix) for another fifteen minutes. Then the nitrogen tubes were elevated above the styrene surface and the 5 parts of S. F. flakes were brushed into the bottles. After passing nitrogen over the surface for another minute a trace of soap was placed on the lip of the bottle which was then sealed. Curves obtained with 2 and $^1/_2$ persulfate are shown in Fig. 1. This simple technique, which removes all but a trace of air, was sufficient to cut the induction period with 2 and $^1/_2$ persulfate to about three minutes at 50°. Since some time must be allowed for warming of the charge from room temperature to 50° and in view of the imperfect technique for removing the oxygen dissolved in the liquid phases, we conclude that in the experiments described, the only cause of an induction period is air (oxygen). When the air was removed only from the gas phase the induction period with $^1/_2$ persulfate was about one hour instead of 0.05 hour when air was removed from both the liquid and gas phases. When the liquid phases originally were saturated to air and in addition the gas phase was air, the induction period was about 3.2 hours with $^1/_2$ persulfate.

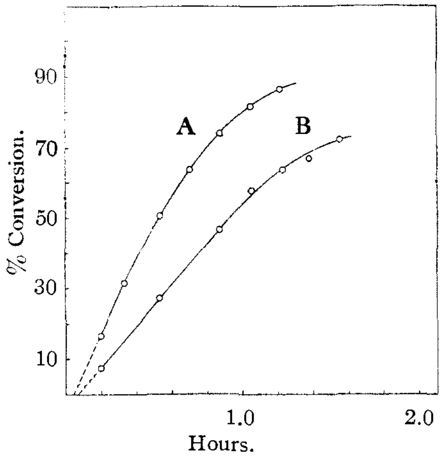

Fig. 1.—Induction periods in absence of air (oxygen): A = 2 $K_2S_2O_8$. B = $^1/_2$ $K_2S_2O_8$.

Effect of Persulfate Concentration on Induction Period.—The length of the induction period was determined as a function of the persulfate concentration. The liquid phases had been exposed to air and the gas phase in each bottle was air. Previously the authors[2] and Price[10] have demonstrated that the concentration of persulfate remains at about 90 to 95% of the original value during the course of styrene emulsion polymerization. Hence the persulfate concentration during the course of the induction period may be considered constant.

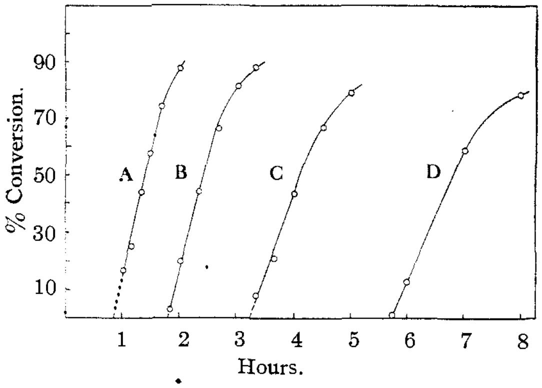

Fig. 2.—Effect of persulfate concentration on induction period caused by air (oxygen), A = 2, B = 1, C = $^1/_2$, D = $^1/_4$, $K_2S_2O_8$.

The conversion data are plotted in Fig. 2. The values for the induction periods obtained by extrapolation are given in Table I.

TABLE I

INDUCTION PERIODS CAUSED BY A GIVEN AMOUNT OF AIR (OXYGEN) AS A FUNCTION OF PERSULFATE CONCENTRATION

Persulfate concn.	Induction period	K_1[a]
2	0.85	1.7
1	1.8	1.8
$^1/_2$	3.2	1.6
$^1/_4$	5.7	1.4

[a] K_1 is defined by: induction period = K_1 (persulfate)$^{-1}$.

From Table I it appears that the induction period is inversely proportional to the persulfate concentration with a given amount of air in the charge and at a given initial partial pressure of oxygen.

Effect of Various Amounts of Air (Oxygen, at the Same Initial Pressure) on the Induction Period.—In order to test the effect of varying amounts of oxygen at the same initial pressure in the charges, 3 bottles were used each of which had a total volume of 253 ml. The bottles were charged as follows: (1) 210 ml. charge of standard recipe with "2" persulfate, liquid phases air saturated, gas phase = 43 ml. nitrogen; (2) as 1, except that gas phase = 43 ml. air; (3) as 2 except $^1/_2$ volume of liquid phases was used. Volume of air saturated charge = 105 ml., gas phase = 148 ml. air. This is equivalent to a 210 ml. air saturated charge with 296 ml. air. In a fourth experiment conditions were equivalent to a 210 ml. charge containing 127 ml. air. The results of the experiments are shown graphically in Fig. 3.

In Table II we list the induction periods obtained by extrapolation of the conversion lines. In the column "Induction Period Caused by Original Gas Phase" the induction periods are given corrected for the induction period caused by the dissolved air in the liquid phases (0.65 subtracted from figures in column 4).

It is evident from Table II that for a given initial partial pressure of oxygen, the induction period is proportional to the amount of air in the charge. There is reasonable agreement of the constants in the two sets of experiments considering that complete air saturation might not have been attained in the different batches of styrene used in sets A and B after distillation. The constant is cal-

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(10) C. C. Price and C. E. Adams, THIS JOURNAL, **67**, 1674 (1945).

Table II

Induction Periods *vs.* Different Volumes of Air at the Same Initial Partial Pressure of Oxygen

Expt.	Bottle	Volume of air above charge	Induction period, hours	Induction period caused by original gas phase	Hours of induction period per ml. of air × 10^{-2}
A	1	0	0.65	0	...
	2	43	1.57	0.92	2.1
	3	296	7.08	6.43	2.2
B	1	0	0.65	0	...
	2	43	1.40	0.75	1.7
	3	127	3.15	2.50	2.0
	4	296	6.50	5.85	2.0

culated assuming that the induction periods caused by the air dissolved in the liquid phases is the same in all the experiments and independent of the volume of the liquid phases.

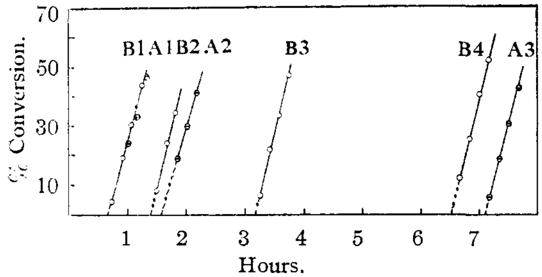

Fig. 3.—Effect of various amounts of air (oxygen) on induction period (see Table II).

Effect of Soap Concentration on the Induction Period.—All the experiments were conducted at the same initial partial pressure and with the same amount of oxygen (air) using the "standard" recipe with 2 persulfate but with varying amounts of soap. The soap was brushed into the bottles from small aluminum boats just before sealing in order to eliminate any possibility that preformed soap solutions of varying concentrations would solubilize different amounts of air. Sampling was begun at the appearance of the blue tinge in the latex. The lack of precision of some of the conversion data is attributed to some precoagulation observed with small amounts of soap. The conversion data obtained without soap in the presence of 2.68% borax are only approximate since the emulsion was not stable enough to withdraw a uniform sample. In the absence of both buffer and soap the emulsion was stable for precise sampling. The conversion data and the corresponding induction periods are shown in Fig. 4 and 5. Evidently the induction periods are practically independent of the amount of soap. They varied from 0.7 hour with 1 soap (5 parts) to 1.1 hour with $^{1}/_{16}$ soap. An induction period of one hour was found without any soap present.

Effect of Oxygen Pressure.—It was anticipated that the rate of disappearance of oxygen would be independent of the oxygen pressure in the charge. This is not true as shown by the following experiment.

The liquid phases in each of three bottles were air saturated. The gas phase of one was flushed with pure nitrogen, the second with air, and the third with pure oxygen. If the induction period were proportional to the amount of oxygen present in the original charge, and independent of the initial oxygen pressure, the induction period observed in the oxygen flushed bottle would be roughly five times that in the air-flushed bottle, taking into account the effect of dissolved air in the liquid phases (see previous section).

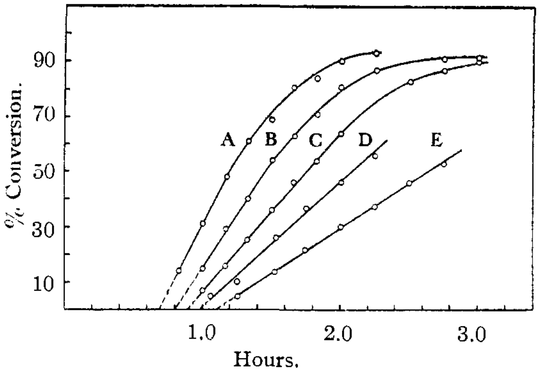

Fig. 4.—Effect of amount of soap on induction period caused by air (oxygen): A = 1, B = $^{1}/_{2}$, C = $^{1}/_{4}$, D = $^{1}/_{8}$, E = $^{1}/_{16}$, soap.

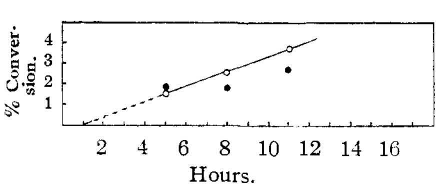

Fig. 5.—Induction periods in absence of soap: -O-O, 0.6% $K_2S_2O_8$; ●, 0.6% $K_2S_2O_8$, 2.68% borax.

The data are plotted in Fig. 6 for 1 persulfate and in Fig. 7 for 2 persulfate. Only one value of conversion for each of the duplicate oxygen-flushed bottles could be obtained because the vacuum prevented removal of the latex by the syringe. Hence after the appearance of the blue tinge the bottles were opened and then sampled. The approximate induction periods were obtained by drawing conversion lines parallel to the others.

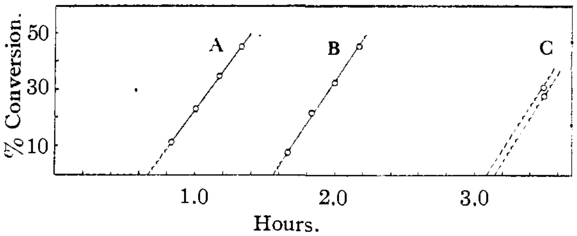

Fig. 6.—Effect of oxygen pressure with 1 $K_2S_2O_8$: gas phase in A, nitrogen; B, air; C, oxygen.

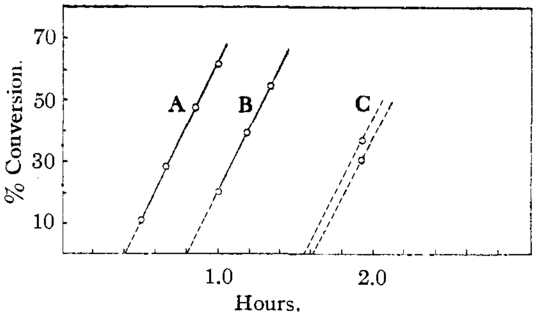

Fig. 7.—Effect of oxygen pressure with 2 $K_2S_2O_8$: gas phase in A, nitrogen; B, air; C, oxygen.

Using 1 persulfate, the induction period in the charge flushed with oxygen was 2.44 hours after correction for dissolved air, and in the air-flushed bottle was 0.90 hour. For 2 persulfate, the oxygen-flushed charge had an induction period of 1.20 hours and the air-flushed charge 0.4

hour. Thus the ratio was approximately 3 instead of 5 as calculated on the assumption that the induction period is independent of the oxygen pressure.

Disappearance of Oxygen in Absence of Persulfate.—Oxygen disappears to an appreciable extent by direct reaction with some constituent of the emulsion in the absence of persulfate. A persulfate-free latex, made with peroxide-free soap, was rotated with a given amount of air at 50° and persulfate was injected after various periods of rotation. When $^1/_2$ persulfate was injected after ten minutes rotation an induction period of about three hours was observed after injection. When the persulfate was injected after two hours of rotation, the induction period after injection was 90% of the original value, and after seven hours rotation, the induction period after injection was 60% of the original value. Extrapolation of the above data would yield an induction period of about twenty hours caused by the given amount of oxygen in the persulfate free charges.

Discussion

All other conditions being the same, it has been found that the induction period in the emulsion polymerization of styrene caused by a given amount of air (oxygen) is inversely proportional to the concentration of persulfate, within a certain range of concentrations, and that no "normal" polymerization of styrene occurs until practically all of the oxygen has disappeared from the charges. Qualitatively, the disappearance of oxygen is accounted for by the following mechanism. The persulfate reacts with styrene in the aqueous phase with formation of activated styrene molecules denoted as M^*. It is well known that oxygen reacts readily with free radicals with formation of peroxides. Conant[11] and Ziegler[12] studied the dependence of oxygen pressure on the rate of reaction with hexasubstituted-ethane types of compounds such as the 9,9′-dialkyldixanthyls. The results were consistent with the view that the rate of reaction of oxygen with free radicals is very rapid, compared with the rate of formation of active centers by dissociation. It may be safely assumed that the rate of activation of styrene is considerably smaller than the rate of reaction of oxygen with free radicals. This is substantiated by the fact that large induction periods are obtained with oxygen in the absence of persulfate. Under these conditions the activation of styrene by persulfate undoubtedly is the rate determining step. Hence the rate of disappearance of oxygen and the lengths of the induction periods are determined by the rate of activation.

(1) $K_2S_2O_8 + M \longrightarrow M^*$ (activated styrene molecule)
(2) $M^* + O_2 \longrightarrow M(O_2)^*$

$M(O_2)^*$ may react in various ways with the constituents of the emulsion.

In the interpretation of the effect of persulfate concentration on the rate of polymerization the assumption has been made[2] that the rate of activation of styrene is proportional to the persulfate concentration. In agreement with this assumption it is found in the present work that the induction period caused by oxygen is inversely proportional to the concentration of persulfate, indicating that the rate of activation of styrene by persulfate during the induction period is the rate determining step.

The oxygen used up during the induction period is not accounted for by peroxides at the end of this period, only a trace of peroxide being found. The reason is that the peroxides are unstable[13] and decompose, and also that a fraction of peroxide formed disappears by acting as a "catalyst" in the activation of styrene molecules. This probably accounts partly for the fact that with a constant amount of oxygen, but decreasing concentrations of persulfate, the induction period is found shorter than corresponds to a value proportional to the reciprocal of the persulfate concentration. Another reason that the induction period is not strictly inversely proportional to the persulfate concentration is that the decrease of persulfate concentration during the induction period becomes relatively greater with decreasing concentrations of persulfate.

The entire mechanism of the disappearance of oxygen during the induction period is not yet clear. If reaction (1) is the rate determining step one would expect that the rate of disappearance of oxygen would be a zero order reaction. Ziegler[12] in his work attributed certain deviations from the zero order dependence of the oxygen reaction to the occurrence of chain reactions.

In the present work we find an apparent zero order reaction of oxygen during the induction period when the initial pressure of oxygen in the charges is kept constant. However, the rate of disappearance of oxygen has been found to be dependent upon the initial oxygen pressure. Therefore the "over-all" reaction giving the consumption of oxygen during the induction period is not a zero order one. The effect of the efficiency of stirring of the reaction mixture upon the rate of oxygen uptake is being studied now.

In the interpretation of the mechanism of the oxygen induction period it should be realized that oxygen is consumed slowly by a persulfate-free charge.

The most interesting result of this study is that the induction period is found to be hardly dependent upon the amount of soap in the charge. This shows clearly that the soap micelles play only a subordinate part during the induction period. Most of the styrene present in the aqueous phase is solubilized in the soap micelles and only a small fraction is molecularly dissolved in the "pure" water. By varying the amount of soap in the recipe the total amount of styrene in the aqueous phase varies almost in proportion to

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(11) Conant, *et al.*, THIS JOURNAL, **47**, 572, 3068 (1925); **48**, 1743 (1926); **49**, 2080 (1927); **51**, 1925 (1929).

(12) Ziegler, Seib, Knoevenagel, Herte and Andreas, *Ann.*, **551**, 150–186 (1942); Ziegler, Orth, Weber and Ewald, *ibid.*, **479**, 277 (1930); **504**, 131, 182 (1933).

(13) See, *e. g.*, S. Medvedev and P. Zeitlin, *Acta Physicochim. U. R. S. S.*, **20**, 3 (1945).

the amount of soap. From the fact that the amount of soap hardly affects the length of the induction period we conclude that mainly the styrene molecules dissolved in the water are activated by the persulfate during the induction period and that the solubilized styrene in the soap micelles plays a subordinate role during this period. Hence the locus of the activation of the styrene is mainly the "pure" aqueous phase, and, to a considerably smaller extent, the soap micelles.

It should be realized that the rate of polymerization of the styrene after the induction period depends on the soap concentration. From the experiments given in Fig. 4 we conclude that the rate of polymerization of styrene is proportional to the square root of the soap present in the charge. This matter is being studied further.

Acknowledgment.—The authors acknowledge the help of Miss Julie M. Schott, who assisted in the experiments.

Summary

1. The induction period caused by oxygen in the emulsion polymerization of styrene using persulfate as "catalyst" is inversely proportional to the persulfate concentration, and, provided that the initial partial pressure of oxygen is constant, the induction period is found proportional to the amount of oxygen. Under these conditions the disappearance of oxygen is determined by the rate of activation of styrene molecules, which is proportional to the concentration of persulfate. It has been established that under the experimental conditions the disappearance of oxygen is not a zero order reaction when the initial pressure of oxygen is varied.
2. The length of the induction period is hardly dependent upon the amount of soap in the charge. This indicates that during the induction period mainly styrene molecules dissolved in the "pure" water are being activated by persulfate and that the styrene solubilized in the soap micelles plays a subordinate part in the reaction during the induction period.
3. The rate of polymerization is proportional to the square root of the amount of soap in the recipe.
4. Oxygen acts like a temporary shortstop.

MINNEAPOLIS, MINNESOTA RECEIVED MAY 8, 1946

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Polarography of Uranium. III. Polarography in Very Weakly Acid, Neutral or Basic Solution[1]

BY W. E. HARRIS AND I. M. KOLTHOFF

In moderately acid solution there are two polarographic reductions of uranium,[2] the first corresponding quantitatively to the reduction of hexavalent uranium to the pentavalent state and the second to the reduction to the trivalent state. This paper will be confined to a discussion of the polarography of uranyl in solutions containing only slight traces of free acid, no free acid or slight amounts of alkali, and to the polarography of uranyl in carbonate solutions.

Early work[3] on the polarography of uranium in slightly acid or neutral solution is scanty and inconclusive.

A recent note by Heal[4] on the polarography of uranium in weakly acid medium is in substantial agreement with our work reported previously and in the present paper.

Strubl[5] investigated the polarography of the complex formed between uranyl and a large excess of ammonium carbonate. He found two reduction waves of uranium of equal magnitude at about −0.8 and −1.4 v. *vs.* the saturated calomel electrode. Without conclusive evidence he states that the first wave is due to the reduction of the uranyl carbonate complex to the tetravalent state and that the second wave is due to reduction to the bivalent state.

In this paper it is shown that the polarographic reduction waves of nearly neutral uranyl solutions are strongly affected by hydrolysis of the uranyl ion.

$$UO_2^{++} + H_2O \longrightarrow UO_2OH^+ + H^+ \qquad (1)$$

At all acidities[2] the reduction corresponding to the first wave with a half-wave potential of −0.18 v. is

$$UO_2^{++} + e^- \longrightarrow UO_2^+ \qquad (2)$$

If the reduction according to equation (2) is more rapid than the re-establishment of hydrolysis equilibrium according to equation (1) the magnitude of the first wave should correspond to the amount of unhydrolyzed UO_2^{++} present in the original solution. Actually this has been found to be true.

In solutions of uranyl chloride without excess of free acid and in solutions of uranyl chloride to which small amounts of alkali have been added, UO_2^+, formed during the first reduction, and UO_2OH^+ are reduced (equations 3 and 4) to-

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[1] From a thesis submitted by W. E. Harris to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, June, 1944.

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