p-xyloquinone, duroquinone, diduroquinone, chroman-5,6-quinone and rancid lard have been determined and compared with their spectra in alkaline solution.

2. Diketostearic acid in alkali may give rise to a quinone homologous to duroquinone.

3. The alcoholic alkali color of rancid fats is probably not due to the formation of para quinones from α-dicarbonyl compounds formed during the oxidation of the fat.

4. The alcoholic alkali color is only to a very small extent due to chroman-5,6-quinone derived from tocopherol or its degradation products in alkali.

5. The alcoholic alkali color may to an appreciable extent be due to compounds derived from the unsaturated fatty acids which are closely related to the compounds obtained from chroman-5,6-quinone by treatment with alkali.

6. The alcoholic alkali color may largely result from other unsaturated carbonyl compounds which are oxidation products of unsaturated fatty acids.

MINNEAPOLIS, MINN. RECEIVED JUNE 8, 1945

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

The Mechanism of Emulsion Polymerizations. I. The Effect of Persulfate Concentration in the Emulsion Polymerization of Styrene[1]

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

The mechanism and the kinetics of the bulk polymerization of styrene and various other vinyl compounds and of solutions of such compounds have been studied by various workers.[2] In general it has been found that, within wide limits, the rate of conversion is proportional to the square root of the "catalyst" concentration. The "catalyst" actually is an initiator and not a catalyst. It is generally an oxidizing agent, such as benzoyl peroxide or substituted peroxide. It is assumed that the "catalyst" dissociates into free radicals which, in turn, react with the monomer. The unstable reaction product of the free radical and the monomer initiates the chains by reacting with more monomer molecules. Thus

$$A_2 \longrightarrow 2A\cdot \quad \text{(Dissociation of "catalyst")} \qquad (1)$$

$$A\cdot + M \longrightarrow AM\cdot \quad \text{(Formation of activated monomer)} \qquad (2)$$

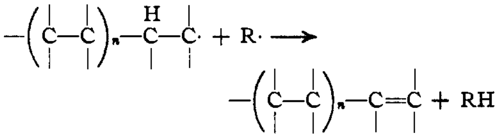
$$AM\cdot + nM \longrightarrow AM\cdot_{n+1} \quad \text{(Chain initiation and propagation)} \qquad (3)$$

That the "catalyst" participates in the polymerization reaction was shown to be true by Price, *et al.*,[2a] and Pfann, Salley and Mark.[2d] Working with *p*-bromobenzoyl peroxide as a "catalyst," Price found from one-half to two and one-half groups derived from the peroxide per polymer molecule, while Pfann, *et al.*, report between one and three such groups per terminated chain.

According to the classical view, termination of the active chains occurs either by reaction with other active chains and with simple free radicals

$$R_n^\cdot + R_m^\cdot \longrightarrow R_nR_m \qquad (4)$$

in which $R_n^\cdot$ and $R_m^\cdot$ represent any activated molecule, from a growing polymer chain to a simple free radical, or by disproportionation



$$-\left(\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\right)_n-\overset{H}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + R\cdot \longrightarrow -\left(\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\right)_n-\underset{|}{C}=\overset{|}{\underset{|}{C}} + RH \qquad (5)$$

The rate of formation of free radicals (6) is proportional to the "catalyst" concentration. Assuming a steady state, this rate of formation is equal to the rate of destruction of free radicals (7).

$$d[A\cdot]/dt = k_1[\text{cat}] \quad \text{(Rate of formation)} \qquad (6)$$

$$-d[A\cdot]/dt = k_2[A\cdot]^2 \quad \text{(Rate of destruction)} \qquad (7)$$

Then, at the steady state

$$[A\cdot] = k_3[\text{cat}]^{1/2} \qquad (8)$$

In single phase vinyl polymerizations, the overall rate of polymerization is then given by (9)

$$-d[M]/dt = k_4[A\cdot][M] = k[\text{cat}]^{1/2}[M] \qquad (9)$$

In the present paper it is shown that the kinetics of the emulsion polymerization of styrene with potassium persulfate as the "catalyst" can be accounted for on the basis of the above classical mechanism. This is true both in the absence and presence of a chain transfer agent. Since the monomer remains as a separate phase until a relatively high conversion, an *apparent* zero order reaction with regard to the monomer is found until all of the monomer disappears as a separate phase and is dissolved in the polymer particles.

Experimental

In subsequent papers it will be shown that oxygen causes a typical induction period in the emulsion polymerization of styrene and also in the emulsion copolymerization of butadiene and styrene. The length of the induction period increases with the amount of oxygen present and it was found to be inversely proportional to the amount of

---

(1) Published with permission of Rubber Reserve Company, Washington, D. C.

(2) (a) C. C. Price, THIS JOURNAL, **64**, 1103, 2508 (1942); (b) Price and R. W. Kell, *ibid.*, **63**, 2798 (1941); (c) Price and B. E. Tate, *ibid.*, **65**, 517 (1943); (d) H. F. Pfann, D. J. Salley and H. Mark, *ibid.*, **66**, 983 (1944); (e) W. Kern and H. Kammerer, *J. prakt. Chem.*, **161**, 81 (1942); (f) G. V. Schultz and E. Husemann, *Z. physik. Chem.*, **B39**, 246 (1938); (g) A. C. Cuthbertson, G. Gee and E. K. Rideal, *Proc. Roy. Soc.* (London), **A170**, 300 (1939); (h) R. G. W. Norrish and E. F. Brookman, *ibid.*, **A171**, 147 (1939); (i) H. W. Melville, *Ann. Repts. Chem. Soc.* (London), **36**, 61 (1939).

persulfate used as the "catalyst" in the recipe. The oxygen disappears during the induction period and no polymerization occurs if the polymerization mixture is stirred or shaken efficiently. During the induction period, a part of the oxygen is transferred into substances with a peroxidic character. It appears that the peroxidic compounds are decomposed again during the induction period but traces of peroxidic compounds were always found at the end of the induction period and these compounds act as "catalysts" in the polymerization.

In order to obtain conclusive results, the experiments described below were carried out in vacuum. As reaction vessels, H-tubes were used which were sealed under vacuum after the oxygen had been expelled from the solutions.[3]

Reagents

Styrene.—C. P. Monsanto styrene, containing 10 p. p. m. of *t*-butylcatechol, was fractionated *in vacuo*. The constant boiling fraction was used immediately after the distillation.

Palmitic Acid.—A pure product of palmitic acid free of unsaturates was obtained from Professor W. M. Lauer of the University of Minnesota.

Potassium Persulfate.—C. P. potassium persulfate was recrystallized twice from conductivity water and dried *in vacuo* at room temperature to constant weight.

Potassium Palmitate.—The soap was prepared (*in situ*) in the apparatus described below by mixing the oxygen-free solution of palmitic acid in the styrene with the oxygen-free solution of 0.184 *N* potassium hydroxide in conductivity water.

The charges were composed of 40.85 ml. of a solution of 21.38 g. of palmitic acid in 500 ml. of styrene, 11.7 ml. of conductivity water, 36.4 ml. potassium hydroxide solution, and 15.7 ml. persulfate solution of a given concentration.

The solution of the palmitic acid in styrene was placed in one leg of an H-tube and the aqueous solution of the other constituents was placed into the other leg. The tubes were then evacuated and filled with purified nitrogen, this process being repeated several times. It was not always possible to prevent bumping of the solutions at low pressures. After the last evacuation, the tubes were finally sealed *in vacuo*. The tubes were rotated end over end at 35 r. p. m. at 30.0°. This temperature was selected because it was found to give a convenient rate of conversion.

In these experiments the soap was prepared *in situ*, *i. e.*, at the time of mixing the styrene and aqueous phases, because, as a result of foaming during evacuation, it was found impossible to make a preformed soap solution oxygen-free.

After rotation for a given period of time the tubes were cooled immediately in ice and then opened for the determination of conversion. In order to prevent further polymerization, 0.1% hydroquinone (based on total monomer content) was added. Separate experiments showed that in the presence of this amount of hydroquinone no further polymerization occurred during the removal of water and styrene from the latex. A weighed sample of latex containing a trace of hydroquinone was evaporated at 80°, to constant weight. Additional drying at 50° *in vacuo* did not result in further decrease of the weight. From the composition of the charge the per cent. conversion of the monomer is readily calculated. With a given latex the conversion could be duplicated easily within 1%.

Reproducible results were obtained with persulfate concentrations varying between 0.0062 and 0.062 molar (referred to the total volume of the aqueous phase). Experiments with lower concentrations of persulfate than 0.0062 *M* were badly reproducible. In the emulsion polymerization of styrene at 30° more than 90% of the persulfate was found unused after six hours. Hence, for all practical purposes, we may consider that the persulfate concentration remains constant during the polymerization under the present experimental conditions.

TABLE I

THE EFFECT OF PERSULFATE CONCENTRATION ON THE RATE OF CONVERSION OF STYRENE (IN THE ABSENCE OF OXYGEN) (TEMP., 30.0°)

Expt.	Total vol. of charge, ml.	Persulfate concn., *M*	Time, hrs.	Conversion, %	Rate, av. per hr.
1	100.6	0.0310	1	28	
			2	56	28
2	100.6	0.0062	2	24	
			3	43	13
			4	52	
3	64.0	0.062	0.5	18	
			1	37	35
			1.5	50	
4	64.0	0.0310	1	24	
			2	56	26
5	64.0	0.0062	1	18	
			2	30	15
			3	38	

Experiment 3 shows that under the specified experimental conditions the rate of conversion is practically constant up to 50% conversion. It can be concluded from these data that the rate of conversion of styrene is proportional to the square root of the persulfate concentration. Using the expression $V = k(P)^{1/2}$ where V is the rate of conversion of styrene at 30°, k is a constant, and (P) is the persulfate concentration, we calculate from experiment 4 that the rate of conversion in experiment 3 should be 37%. The experimental value is 35% per hour. The calculated value for experiments 2 and 5 is 12%, whereas the actual varied between 13 and 15%.

In regard to the concentration of "catalyst," equations 6, 7 and 8 account equally well for the emulsion polymerization of styrene as for the bulk polymerization of styrene.

From viscosity measurements of polymers prepared with widely varying concentrations of persulfate it was concluded that persulfate is not a chain transfer agent.

It was of interest to investigate how a substance which acts like a chain transfer agent affects the rate of emulsion polymerization. Designating the chain transfer agent as TH, the transfer of chain activity is given by the equations

$$R\cdot_m + TH \longrightarrow R_mH + T\cdot \qquad (10)$$

$$T\cdot + M \longrightarrow TM\cdot \qquad (11)$$

According to this formulation the total number of free radicals at any time, either $R_m^{\cdot}$ or A·, etc., or T·, remains unaffected by the transfer of chain activity. Hence, it was anticipated that the chain transfer agent should not affect the rate of polymerization of styrene.

In a review article "Industrial Progress in Synthetic Rubberlike Polymers," Cramer[4] described a number of substances which act as chain transfer agents, such as mercaptans, thiouram disulfides, and xanthogen disulfides. Fryling[5] in the emulsion copolymerization of butadiene with styrene mentioned isohexyl mercaptan as a chain transfer agent. Price and Adams[6] used *n*-dodecyl mercaptan and found it to be an efficient chain transfer agent. In our experiments we also used *n*-dodecyl mercaptan, a pure sample of which was obtained from Professor C. S. Marvel of the University of Illinois. Intrinsic viscosity measurements have shown that this substance is an effective chain transfer agent in the emulsion polymerization of styrene. For example, using a persulfate concentration equal to 0.0062 *M*, the intrinsic viscosity varied between 6 and 7 at conversions between 25 to 50%. Adding 0.5 g. of *n*-dodecyl mercaptan per 100 g. of styrene at the same persulfate concentration gave polymers with intrinsic viscosities of the order of one at conversions of 50–70%.

Experiments were carried out at 50° varying the amount

---

(3) Compare K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1925).

(4) H. I. Cramer, *Ind. Eng. Chem.*, *Ind. Ed.*, **34**, 243 (1942).

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

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

of mercaptan between the limits of zero and 2.0 parts per 100 parts of styrene. The vacuum technique was not used in this set of experiments but the polymerization cells were flushed thoroughly with purified nitrogen. Varying the concentration of the mercaptan between the limits given above had only a slight effect on the rate of conversion. When 2.0 parts of mercaptan per 100 of monomer was used a slight decrease in the rate of conversion was found. The chain transfer agent in this high concentration acts like a typical diluent of the monomer.

Vacuum experiments were carried out in the H tubes at 30° at a persulfate concentration of 0.0062 *M* using 0.5 part of *n*-dodecyl mercaptan. In the absence of mercaptan a conversion rate of 12.4% per hour was found and with 0.5 part of mercaptan (per 100 parts of styrene) a rate of 14.8% per hour was obtained.

It may be emphasized again that these results refer to the polymerization of styrene alone. In the copolymerization of butadiene and styrene the situation is quite different. The kinetics of the emulsion copolymerization of butadiene and styrene cannot be accounted for by the classical mechanism which is found to hold true for styrene.

Summary

The rate of emulsion polymerization of styrene has been investigated in the absence of oxygen at 30°. It was found that the rate of conversion is proportional to the square root of the concentration of persulfate which was used as the "catalyst." In this respect the kinetics of the emulsion polymerization of styrene is comparable to that of the bulk polymerization.

At a given persulfate concentration the rate remains unaffected by the presence of a chain transfer agent like mercaptan when the concentration of the latter varies between zero and two parts per 100 parts of styrene. This was anticipated on the basis of the classical picture of the bulk polymerization of styrene.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 18, 1945

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Kinetics of the Emulsion Polymerization of Styrene

BY CHARLES C. PRICE AND CLARK E. ADAMS

Since the most-widely used and important technique of vinyl polymerization has become that carried out in emulsion, a study of the emulsion polymerization of styrene was undertaken in order to extend the understanding of the mechanism of this reaction. Styrene was chosen for the single monomer component since it is easily handled and has been extensively studied. The investigation reported herein has revealed that the rate of polymerization of styrene in emulsion is independent of the total styrene content of the emulsion, *i. e.*, that it follows "zero order" kinetics, for at least the first 60 to 75% of the reaction. This contrasts with the first order dependence on monomer for the polymerization of *d*-*s*-butyl α-chloroacrylate[1a] and the three-halves order dependence on monomer for the polymerization of styrene[1b] in solution, each catalyzed by benzoyl peroxide. However, since the polymerization of styrene in emulsion has nearly the same activation energy as in solution and since the rate is in each case dependent on the square root of the catalyst concentration, it seems likely that both proceed through essentially the same type of mechanism, the independence of the rate of emulsion polymerization on the total styrene content of the emulsion being interpreted as evidence in support of the suggestion of Fikentscher and others[2] that emulsion polymerization actually proceeds in the aqueous phase and not in the monomer droplets.

Experimental

The apparatus used in this study was a 1-liter, round-bottomed flask having three ground-glass openings. In these openings were fitted, with corresponding ground-glass joints, a gas-inlet tube with thermometer, an all-glass stirrer with a close-fitting ground-glass bearing, and a sampling tube reaching to the bottom of the reaction flask, with two stopcocks, one to release the pressure in the flask and the other to withdraw samples of latex. This apparatus allowed the reaction to be run under a nitrogen atmosphere at a pressure about 5 cm. of mercury above atmospheric. Under this pressure samples of the latex could be removed rapidly by opening the stopcock of the sampling tube. After the sample was collected, the pressure in the flask was released by opening the stopcock to the outside, and the sampling tube and its tip were then cleared by flushing with nitrogen. It required approximately ten seconds to withdraw the usual 10-cc. sample. The polymerization apparatus was immersed in an oil-bath which was maintained within ±0.1° of the temperature required.

The fatty acid from which the soap was made was prepared by several crystallizations of U. S. P. stearic acid, m. p. 56–57°. The neutral equivalent of this acid was 263 ± 2, so that the 8-g. sample (0.0304 mole) was 87.5% neutralized by the 400 cc. of 0.0666 *N* alkali (0.0266 mole) used in the polymerizations. To avoid interference with the bromine titration, the fatty acid used was necessarily essentially saturated, with an iodine number of less than one. The active oxygen content of this fatty acid was quite low, 3.3 parts per million. An increase in the active oxygen content to 848 parts per million by passing oxygen through the molten fatty acid at 120° only slightly affected the rate of reaction (Table I, expts. 18 and 19).

The catalyst, potassium persulfate, was added as a standard aqueous solution prepared from recrystallized and dried commercial product. The persulfate used was 100% pure, as measured by its peroxide content.

"Chemical" styrene was prepared from pure α,β-dibromoethylbenzene (m. p. 73–74°) by treatment with magnesium according to the method of von Braun and Moldänke.[3]

---

[1] (a) Marvel, Dec and Cooke, THIS JOURNAL, **62**, 3499 (1940); Price and Kell, *ibid.*, **63**, 2798 (1941); (b) Schulz and Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

[2] (a) Fikentscher, *Z. angew. Chem.*, **51**, 433 (1938); (b) Fryling and Harrington, *Ind. Eng. Chem.*, **36**, 114 (1944); (c) Vinograd, Fong and Sawyer, Abstracts, 108th Meeting of the Am. Chem. Soc., New York, N. Y., September 13, 1944.

[3] von Braun and Moldänke, *Ber.*, **54**, 618 (1921).