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).

"Research" styrene was prepared from commercial styrene which was first washed with 10% sodium hydroxide to remove the inhibitor and then vigorously stirred with Nessler reagent. The latter was prepared by the addition of a solution of 245 g. of potassium iodide in 245 cc. of water to a mixture of 100 g. of mercuric chloride and 188 cc. of 10% potassium hydroxide. This process was reported by Johnson and McEwen[4] to remove phenylacetylene, present in commercial styrene. This product was dried with calcium chloride and fractionated under reduced pressure. The center fraction, boiling at 46° (20 mm.), was collected in a receiver suitable for redistillation. This fraction was then heated in the flask under a nitrogen atmosphere at 100 ± 5° for about three hours, which is reported[5] to polymerize 10 to 15% of the styrene. A constant-boiling fraction was collected by distillation of this viscous solution.

The polymerization reaction was always carried out in the same way except for changes noted in special runs. Four hundred cubic centimeters of 0.0666 N potassium hydroxide was added to the reaction vessel, which had been flushed with nitrogen. Passage of nitrogen through the solution was continued while equilibrium with the polymerization temperature was attained. The desired amount of persulfate in 10 cc. of water and the fatty acid dissolved in styrene were then added.

Ten-cc. samples of latex were collected in volumetric flasks through the sampling tube. The sample was immediately and quantitatively transferred to a numbered Erlenmeyer flask by rinsing with water and chloroform and kept in an ice-bath until analyzed. Samples could be collected in this way every four or five minutes and were usually collected as often as possible after the polymerization had started. The end of the induction period was readily noted by a slight increase in the temperature of the reaction mixture and sampling was continued until the temperature of the reaction mixture had subsided to that of the bath.

The regularity and reproducibility of the results indicate that the polymerization in the portion withdrawn was immediately stopped as the sample was collected due to the contact of the latex sample with air. The results of expts. 11 and 12 (see Table I) demonstrate that air is a most effective inhibitor for the emulsion polymerization of styrene. Since no change in the styrene content of samples was noted with varying time of storage before analysis, the samples were diluted with chloroform and kept in an ice-bath until extracted and titrated.

After the polymerization was completed, each sample was transferred to a small separatory funnel and coagulated with 10 cc. of a solution of 50 g. of sodium chloride and 12.5 cc. of concentrated sulfuric acid in 1 liter of water. The coagulated latex was extracted three times with 20-cc. portions of chloroform and the extracts combined. This chloroform solution was titrated with a standard solution of bromine in glacial acetic acid to an end-point of excess bromine which did not fade on standing.[6] The amount of styrene in solution was calculated from the amount of bromine required.

In a number of runs the concentration of persulfate in the emulsion was followed throughout the course of the polymerization by a ferrous sulfate procedure. The coagulated latex was extracted with chloroform which had been purified by treatment with concentrated sulfuric acid and distillation. The aqueous layer was acidified with 10 cc. of 6 N sulfuric acid, and oxygen was removed by bubbling nitrogen through the solution for ten minutes. A definite volume of standard ferrous sulfate solution was added and the mixture allowed to stand under a nitrogen atmosphere for twenty minutes. The amount of potassium persulfate present was calculated from the amount of ferrous sulfate oxidized, as determined by back titration of the remaining ferrous ion with standard ceric sulfate in the presence of ferrous-phenanthroline indicator.[7]

The pH changes in the emulsion during polymerization were followed by means of a Hellige pH-meter. The calomel electrode of the pH-meter was connected with the sample through a saturated potassium chloride bridge so designed that it could be flushed with salt solution to eliminate plugging of the connection by coagulated polystyrene.

A sample of latex for evaluation of the polymer was collected at the end of each polymerization. This sample was coagulated, the polymer was separated from the water with ether, and washed with alcohol and collected by suction filtration. Samples of the polymer which were used for determining the molecular weight were purified by precipitation four times from a stirred chloroform–ether solution by slow addition of alcohol. The molecular weight of the polymer was estimated viscosimetrically. Kemp and Peters[8] have reported a value of 0.45 × 10^4 for the constant of their equation relating molecular weight to relative viscosity for polystyrene in benzene or chloroform.

$$M = \frac{K \log \eta_r}{C}$$

Since toluene is a much better solvent for the very high molecular weight polystyrene formed in emulsion, we determined a value for the constant in toluene, 0.73 × 10^4, by comparing the viscosities of solutions of several polystyrene samples in chloroform and in toluene.

Discussion

In order to evaluate properly the experimental results on the kinetics of the emulsion polymerization of styrene, it was a matter of interest first to ascertain the sensitivity of the reaction to number of important variables, such as the soap, the monomer purity, the pH, exposure to air and many other factors.

The changes in pH during the reaction were observed in expt. 3. These results, summarized in Fig. 1, are similar to those reported by Fryling and Harrington.[2] It can be seen that the variation in the pH of the latex was not very large during the polymerization reaction, and it was not considered necessary to use a pH regulator in this work.

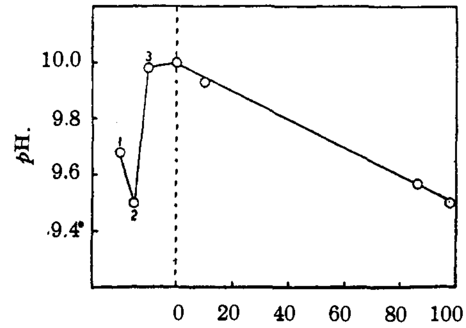

Fig. 1.—Variation of pH with conversion: 1, soap solution; 2, $K_2S_2O_8$ added; 3, styrene added.

The concentration of potassium persulfate in the latex was found to remain more than 95% of

---

[4] Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

[5] Schulz and Husemann, *Z. physik. Chem.*, **B34**, 187 (1936); **B36**, 184 (1937).

[6] Uhrig and Levin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

[7] Private communication from Professor I. M. Kolthoff.

[8] Kemp and Peters, *Ind. Eng. Chem.*, **33**, 1263 (1941); **34**, 1097 (1942).

the initial value throughout the polymerization (expts. 4 and 5, Fig. 2). This variation is hardly more than the experimental error, for samples differed by more than 3% without regard for order. From these results it was concluded that changes in the concentration of persulfate during the course of the polymerization would have no appreciable effect on the rate of reaction.

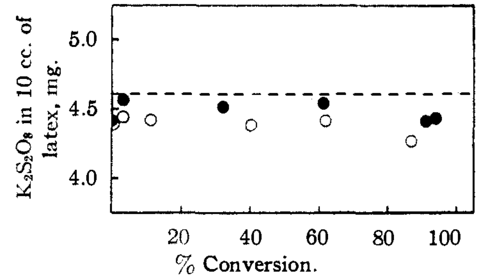

Fig. 2.—Variation of potassium persulfate concentration with conversion: expt. 4, ●; expt. 5, O.

For several polymer samples collected at various per cent. conversions during expts. 1 and 2 (see Fig. 3), the molecular weight was determined viscosimetrically. The results of this investigation indicated that the average molecular weight changed very little during the course of the polymerization. These results are similar to those obtained in the polymerization of styrene in bulk and in solution and support the theory that emulsion polymerization proceeds by a mechanism similar to that proposed for solution and bulk polymerization.

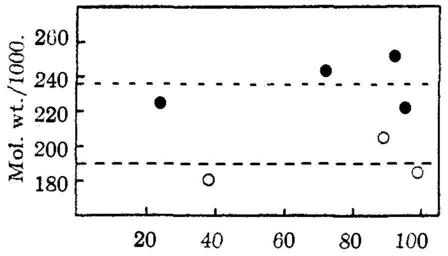

Fig. 3.—Variation of molecular weight with conversion: expt. 1, O; expt. 2, ●.

The equation proposed by Kemp and Peters,[8] with a constant modified for toluene solutions, was used to calculate the "molecular weights" recorded in the tables. The values calculated from this equation are very much lower than those calculated from equations proposed by Staudinger[9] and by Alfrey, Bartovics and Mark.[10] Since the determination of molecular weights from viscosity data is as yet a controversial question, the molecular weights recorded are not intended to be absolute but only to give an indication of the relative degree of polymerization. It is of some interest, however, that the molecular weight of the polymer formed in expt. 9, estimated viscosimetrically to be 256,700, was found to be 285,100 by the osmotic technique of Wall and Beste.[11] Using the Staudinger equation, with a K_m value of 0.5×10^{-4},[9] the viscosity molecular weight would be 2,500,000, and using the equation of Alfrey, Bartovics and Mark,[10] it would be about 6,000,000. The ten- to twenty-fold discrepancy between these viscosity molecular weights and the osmotic molecular weight can hardly be ascribed to a difference between the weight and number average molecular weight of the sample, which, although unfractionated, had been reprecipitated four times.

The viscometric "molecular weight" for the final polymer from each experiment is included in Tables I and II. These values show that the degree of polymerization is decreased as the temperature and catalyst concentration are increased, which is generally observed in polymerization studies. This variation is not very great in emulsion polymerization, and most of the viscometric molecular weights were found to be between 200,000 and 300,000 by the Kemp and Peters[8] equation.

The length of the induction period and the rate of reaction were found to be dependent on the purity of the styrene used. Styrene prepared by debromination of pure α,β-dibromoethylbenzene with magnesium was used as a basis of purity for styrene prepared by other methods; it has been referred to herein as "chemical" styrene. "Research" styrene, obtained by distillation of purified commercial styrene which had been partially polymerized by heat, was found to give the same results as the styrene prepared chemically. This partial polymerization and distillation of styrene otherwise carefully purified increased the rate constant from 0.024 to 0.028 mole styrene/liter of latex/minute[12] and reduced the induction period before the start of the polymerization two- to tenfold (see Table I). It appears that this partial polymerization procedure for preparing "research" styrene removed some inhibitor or retarder which could not be separated completely by washing or distillation.

Although specially purified styrene was used, the induction period could not be completely eliminated or controlled. Experiments 11 and 12 show that an air atmosphere completely inhibits the polymerization reaction. Thus, although the reaction flask was flushed with nitrogen before use and a nitrogen atmosphere was maintained at all times, it is not unlikely that traces of oxygen remained in the flask and in the reagents used and that these traces of oxygen account for the small induction periods observed. It was significant that the rate in expts. 11 and 12, where the induc-

(9) Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932, p. 209.

(10) Alfrey, Bartovics and Mark, THIS JOURNAL, 65, 2319 (1943).

(11) We wish to express our appreciation to Professor F. T. Wall and Mr. L. F. Beste for this determination.

(12) Hereafter the units, mole styrene/liter of latex/minute, will be implied in all the rate values given.

TABLE I

EFFECT OF VARIABLES ON THE EMULSION POLYMERIZATION OF STYRENE AT 50° BATH TEMPERATURE

Expt.	Soap	Mole/l. catalyst	Styrene cc.	Styrene purity	Induction period, min.	k_0 mole l.$^{-1}$ min.$^{-1}$	Mol. wt.
1	Na[a]	0.00406	50	Comm.	105	0.0259	185,200
2	Na[a]	.00448	100	Comm.	89	.0436	222,300
3	Na[a]	.00211	100	Comm.	292	.0219	226,000
4	K	.00203	50	Res.	35	.0265	257,300
5	Na[a]	.00203	50	Chem.	13	.0281	290,700
6	Na[a]	.00203	50	Comm.	230	.0192	248,200
7	Na[a]	.00203	50	Comm.	159	.0194	231,100
8	Na	.00203	50	Comm.	316	.0251	237,400
9	Na	.00203	50	Comm.	46	.0240	256,700
10	K	.00203	50	Res.	23	.0282	269,500
11	K	.00203	50	Res.	1461 (air)	...	....
12	K	.00203	50	Res.	1675 (air)	...	....
					40 (N_2)	.0306	218,400
13	Na, neut.	.00203	50	Comm.	129	.0200	205,300
14	Na, 10% excess alk.	.00203	50	Comm.	33	.0206	228,700
15	Na, 10% excess acid	.00203	50	Comm.	72	.0238	218,400
16	Na	.00203	50	Res.	22	.0280	158,500
17	K	.00203	50	Res.	20	.0282	219,700
18	Na, 848 ppm. act. oxygen	.00203	50	Comm.	37	.0226	223,700
19	Na, 3.3 ppm. act. oxygen	.00203	50	Comm.	36	.0246	246,700
20	K	.00305	50	Res. + 0.5% dodecyl mercaptan	3	.0298	15,400
21	K dehydroabietate	.00305	50	Res.	13	.0115	168,600
47	K dehydroabietate	.00305	50	Res.	14	.0125	171,000
48	K hydro- and dehydroabietate	.00305	50	Res.	17	.0100	145,300

[a] This soap was prepared in aqueous solution previous to experiments, the other samples were prepared *in situ*.

tion period was prolonged to over twenty-four hours by exposure to air, was only very slightly greater than for similar runs conducted in a nitrogen atmosphere, 0.0306 compared with 0.0282. Although it would be preferable to eliminate the induction period, it appears to be of minor importance in determining the rate of polymerization.

The potassium soap of U. S. P. stearic acid, recrystallized from ethanol and prepared *in situ*, was found to be most readily applicable to this study. Latex from potassium soap was more easily handled than that prepared from sodium soap, since the latter was more viscous and tended to form gels on cooling. The rate of reaction was the same when either sodium or potassium soap was used, as is shown in expts. 16 and 17. Soap prepared *in situ*, by the addition of the fatty acid, dissolved in the monomer, to a standard alkali solution, gave more reproducible results and a somewhat faster rate of reaction than addition of monomer to aqueous soap solutions. Experiments 6 and 7, rate 0.019 with soap solution, and expts. 8 and 9, rate 0.024 with soap prepared *in situ*, may be compared in this respect. The results from expts. 13, 14, and 15 showed that the rate of reaction was slightly increased by the use of a 10% excess of fatty acid (0.0238) compared with an equivalent amount of alkali (0.0200) and a 10% excess of alkali (0.0206).

Addition of 0.5%, based on the weight of monomer, of dodecyl mercaptan (expt. 20) had only a slight retarding effect on the rate of polymerization (0.030 compared with 0.035 for expts. 32 and 33), but the viscosity "molecular weight" of the polymer was reduced from about 265,000 (average for expts. 32 and 33) to 15,000. The mercaptan thus acts as a chain transfer agent. The presence of mercaptan also appeared largely to eliminate the induction period.

In expts. 21 and 47, using dehydroabietic acid[13] for the emulsifying agent, the rate of reaction was one-third, and the molecular weight of the polymer six-tenths that of a corresponding experiment with fatty acid. Similar results were obtained using a mixture of hydro- and dehydroabietic acids[13] (expt. 48, Table I).

To evaluate the effect of styrene and persulfate content, as well as temperature, on the rate of the polymerization, a series of experiments was carried out at 40, 50 and 60° in which only the concentration of the two reagents was varied. The zero- and first-order dependence on styrene content are compared in Figs. 4 and 5 for a series of experiments at 50°. This comparison is based on the linear relationship between concentration and time for zero-order kinetics, and between the logarithm of concentration and time for first-order kinetics.

---

(13) Kindly supplied by Hercules Powder Company. The dehydroabietic acid was a purified, crystalline sample, m. p. 167–169°

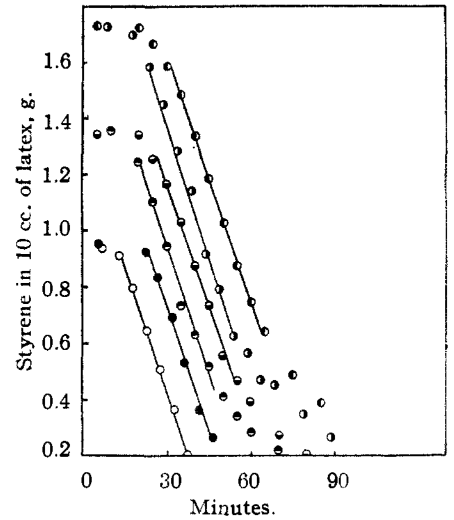

Fig. 4.—Rate of polymerization of styrene at 50°, persulfate 0.00203 mole/liter: expt. 5, ○; expt. 10, ●; expt. 28, ◓; expt. 29, ◒; expt. 30, ◐; expt. 31, ◑.

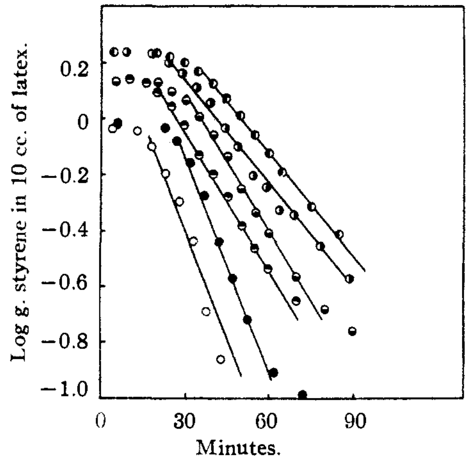

Fig. 5.—Rate of polymerization of styrene at 50° (plotted as a first-order reaction), persulfate 0.00203 mole/liter: expt. 5, ○; expt. 10, ●; expt. 28, ◓; expt. 29, ◒; expt. 30, ◐; expt. 31, ◑.

From the graphs for individual experiments, it is not possible to distinguish definitely between the zero- or the first-order reaction. However, the zero-order points usually fall on a better straight line, the first-order points showing a greater or less tendency to fall on a sigmoidal curve. Furthermore it is observed that, for a given catalyst concentration, the zero-order rate for the reaction remains constant when the concentration of monomer is varied two-fold. The first-order reaction rate, however, is approximately inversely proportional to the monomer concentration. These data are thus convincing evidence for the zero order dependence of the rate on styrene content of the emulsion. Further kinetic data are presented graphically in Figs. 6, 7 and 8 and are summarized in Table II.

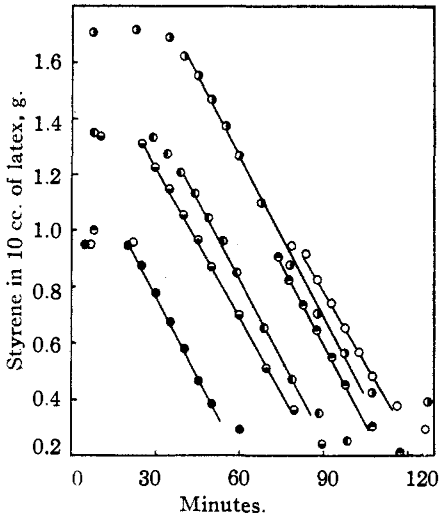

Fig. 6.—Rate of polymerization of styrene at 50°, persulfate 0.00101 mole/liter: expt. 22, ●; expt. 23, ○; expt. 24, ◓; expt. 25, ◒; expt. 26, ◐; expt. 27, ◑.

These zero-order kinetics for styrene polymerization are evidently peculiar to emulsion polymerization; catalytic vinyl polymerization in solution is first-order with respect to monomer concentration.[1a] Since emulsion polymerization is believed to proceed by the same free-radical type mechanism as polymerization in solution, the reaction kinetics observed in emulsion polymerization are probably limited by some factor other than the polymerization reaction itself.

TABLE II

RATES OF EMULSION POLYMERIZATION OF STYRENE AT VARYING MONOMER AND CATALYST CONCENTRATIONS

Expt.	Mole/l. catalyst	Ratio styrene	Max. temp., °C.	k_0	k^a (cor.)		Mol. wt.
42	0.00203	1:8	40.8	0.0101	0.207	40°	235,300
43	.00406	1:8	41.0	.0130	.185		292,700
44	.00406	1:8	41.0	.0122	.174		379,400
45	.00609	1:8	41.5	.0199	.221		306,600
46	.00812	1:8	42.0	.0218	.199		....
22	.00101	1:8	51.3	.0186	.520	50°	314,000
23		1:8	51.0	.0164	.471		352,000
24		1:8	51.4	.0183	.507		290,500
25		1:6	51.0	.0168	.482		301,000
26		1:6	51.0	.0177	.509		332,000
27		1:4	51.2	.0180	.508		375,000
5	.00203	1:8	52.0	.0282	.523		290,700
10		1:8	52.5	.0283	.502		269,500
28		1:6	52.5	.0290	.514		321,000
29		1:6	52.2	.0287	.523		299,300
30		1:4	52.3	.0283	.509		299,300
31		1:4	52.7	.0294	.512		305,200
32	.00305	1:8	52.9	.0352	.512		279,500
33		1:8	52.7	.0344	.488		250,500
34	.00406	1:8	53.0	.0394	.471		269,900
35		1:8	53.2	.0394	.463		238,400
36		1:6	53.1	.0396	.464		226,800
37		1:4	53.4	.0404	.466		258,100
38	.0406	1:8	55.8	.216 (?)	.638		196,200
39	.00203	1:8	64.3	.0642	.987	60°	219,300
40	.00101	1:8	63.7	.0526	1.205		256,700
41	.00051	1:8	62.6	.0344	1.218		271,300

[a] $k = k_0/[\text{cat.}]^{1/2}$. The values reported have been corrected for the observed temperature rise.

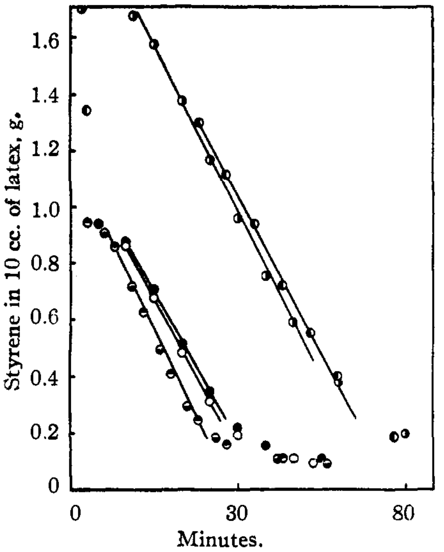

Fig. 7.—Rate of polymerization of styrene at 50°, persulfate 0.00406 mole/liter: expt. 34, ◒; expt. 35, ◓; expt. 36; ◐; expt. 37, ◑; persulfate 0.00305 mole/liter: expt. 32, ○; expt. 33, ●.

These kinetics may be explained on the basis of the suggestion of Fikentscher[2a] that emulsion polymerization proceeds in the aqueous solution of monomer. Thus the reaction would take place in a saturated solution of styrene which would be continually replenished from the monomer droplets as the styrene polymerized. As the rate of polymerization in emulsion is quite rapid, the process of solution of the monomer from the droplets must be extremely rapid, in order to maintain a constant concentration. The purpose of the emulsifying agent might therefore be three-fold. It may serve to subdivide the monomer so that an extremely large surface area would be exposed to water to maintain equilibrium solubility. Secondly, it may considerably increase the equilibrium solubility of the monomer. Thirdly, it may act as a colloid-stabilizer, largely preventing the coalescence of the original monomer droplets with the polymer particles thus maintaining a supply of substantially pure styrene throughout a major portion of the polymerization.

The similarity between emulsion and solution polymerization is substantiated by the relationship of the rate of reaction to the catalyst concentration. Schulz and Husemann[1b] and Price and Kell[1a] have shown that the rate of reaction for vinyl polymerization is proportional to the square root of the catalyst concentration, if the temperature and monomer concentration are held constant.

On this same basis, the kinetics for the emulsion polymerization can be represented as

$$-\mathrm{d}[\mathrm{C_8H_8}]/\mathrm{d}t = k[\mathrm{cat.}]^{1/2}$$

Since the catalyst concentration was shown to remain essentially unchanged during the course of the polymerization, we may write

$$k[\mathrm{cat}]^{1/2} = k_0 \text{ or } k = k_0/[\mathrm{cat}]^{1/2}$$

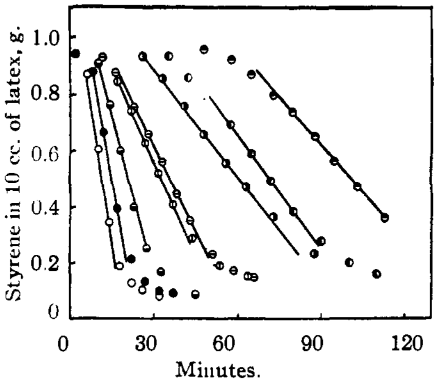

Fig. 8.—Rate of polymerization of styrene, at 40°: expt. 42, ◓; expt. 43, ◐; expt. 44, ◑; expt. 45, ⊖; expt. 46, ⦶: at 60°: expt. 39, ○; expt. 40, ●; expt. 41, ◒.

The actual half-order constant, k, is thus derived from the pseudo-zero order constants, k_0, by dividing the latter by the square root of the catalyst concentration.

In order for these values of k to be directly comparable, it was necessary to correct them for the small temperature rise in each experiment due to the large heat of polymerization. This was accomplished by estimating an approximate energy of activation, $E = 19{,}000$ cal., which was then used in the equation

$$\log k_\mathrm{b} = \log k_\mathrm{a} + \frac{E}{2.303 \times R} \times \frac{T_\mathrm{b} - T_\mathrm{a}}{T_\mathrm{b}T_\mathrm{a}}$$

The average values for the corrected constants at 40, 50 and 60° (see Table II) were then used to calculate the over-all energy of activation for the reaction

$$\ln k = \mathrm{const} \frac{-E}{RT}$$

The physical interpretation of this energy of activation is rather difficult, for in polymerizations a number of reactions are proceeding at the same time. In addition, changes in temperature might affect the solubility relationships in the latex. Our results, however, show that the natural logarithm of the rate constant is indeed linearly dependent upon the inverse of the absolute temperature. Furthermore, the apparent over-all activation energy found, 18,500 ± 500 calories per mole, is in good agreement with the values found for the polymerization of styrene by other techniques, about 20,000 calories per mole.[14]

Summary

A method which gives satisfactory results for studying the rate of polymerization of styrene in soap emulsion has been developed. The polymerization was completely inhibited by air. Under nitrogen, the rate of reaction was found to be independent of styrene content and dependent on the square root of the persulfate catalyst concentration. The concentration of the catalyst was

---

[14] Mark and Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, N. Y., 1941, p. 214.

shown to remain essentially constant during the polymerization. The kinetics are interpreted on the basis that the zero-order dependence of polymerization in emulsion on monomer content is not due to a difference in mechanism from solution polymerization but is limited by the solubility of the styrene in the water phase, within which the polymerization takes place.

Polymerization of styrene emulsified by potassium dehydroabietate or mixed hydro-dehydroabietate gave a somewhat lower-molecular-weight polymer and a slightly slower rate of reaction than emulsification by soaps of high-molecular-weight fatty acid.

Addition of dodecyl mercaptan to the polymerization greatly reduced the molecular weight of the polymer formed, as well as the induction period before polymerization started, but had little effect on the rate of reaction.

URBANA, ILLINOIS RECEIVED JUNE 18, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SYDNEY]

The Polarographic Reduction of Some Cobaltammines and Related Compounds

BY J. B. WILLIS, J. A. FRIEND AND D. P. MELLOR

Although the polarographic reduction of complex metal ions has already been studied to some extent both in theory and in practice,[1a] attention has hitherto been almost entirely confined to complexes in which the coördination sphere of the metal ion contains only one kind of molecule or ion, as in such complexes as $[Co(NH_3)_6]^{+++}$ and $[Fe(CN)_6]^{---}$. Ions such as $[Co(NH_3)_5NO_2]^{++}$, for instance, do not seem to have been studied. One reason for this is that in previous investigations the complex ions have as a rule been formed by the addition of a simple metal salt to a large excess of the coördinating substance, which also acts as supporting electrolyte; no attempt has been made to isolate the substance actually undergoing reduction.

The purpose of the present investigation was to study the reduction of complex ions formed from the hexammine cobaltic ion by progressive substitution of the ammonia molecules by other groups. Complexes with ethylenediamine were also studied. Among the ammines, the nitro-substituted compounds were selected for intensive study because these compounds have been well studied from the point of view of physicochemical properties, and because almost a complete series from $[Co(NH_3)_6]^{+++}$ to $[Co(NO_2)_6]^{---}$ is known, the only missing member being $[Co(NH_3)(NO_2)_5]^{--}$.

Some chloro- and aquo-substituted complexes also were studied.

Theory

Since it was desired to prevent the complexes from undergoing alteration when dissolved, a supporting electrolyte was required which would not tend to coördinate with the metal ion. Normal potassium nitrate was first tried, since the nitrate ion shows great reluctance to coördinate, but maxima were obtained which were very difficult to suppress. Normal potassium sulfate, 0.1 *N* potassium sulfate and 0.1 *N* sodium acetate were used and found satisfactory for different sections of the work. As far as maxima were concerned the ammonia complexes caused much less trouble than complexes containing ethylenediamine. Maxima obtained with the former could be suppressed easily by methyl red, whereas those obtained with the latter often did not respond to this treatment.

That the cobaltammines preserve their identity in aqueous solution is shown by the following: (a) Conductivity measurements have been satisfactorily and reproducibly carried out on them. (b) Each substance gives a characteristic and reproducible polarogram which does not change after the solution has stood for some time. The determination of the number of electrons involved in the polarographic reduction was carried out by the application of the Ilkovič equation.[2] The diffusion coefficient of the ion undergoing reduction was calculated from its equivalent conductivity at infinite dilution as described by Kolthoff and Lingane.[1b]

Experimental

A manual instrument, similar to that previously described,[3] was used.

All measurements were made at 25°; air was displaced from solutions by purified nitrogen. The half-wave potentials ($E_{1/2}$) are relative to the saturated calomel electrode, and are considered to be in error by not more than approximately ±10 mv. They are corrected for the potential drop across the polarographic cell. Methyl red was used as a maximum suppressor, because by experience it was found that, unlike gelatin and methyl cellulose, it does not cause a shift in the half-wave potential.

The substances used were mainly the chlorides of the complex cations, and sodium or ammonium salts of complex anions. They were prepared according to the standard methods of Jörgensen and Werner,[4] and were checked for purity by gentle ignition with a few drops of concentrated sulfuric acid and weighing as anhydrous cobalt sulfate.

The solutions were 0.001 *M* with respect to the ion

---

(1) (a) Kolthoff and Lingane, "Polarography," Interscience Publishing Co., New York, N. Y., 1941, p. 161; (b) Kolthoff and Lingane *ibid.*, p. 44.

(2) Ilkovič, *Coll. Czech. Chem. Comm.*, **6**, 498 (1934).

(3) Willis, THIS JOURNAL, **66**, 1067 (1944).

(4) Jörgensen, *J. prakt. Chem.*, **39**, 8 (1889); *Z. anorg. allgem. Chem.*, **17**, 455 (1898), etc.; Werner, *Ber.*, **39**, 2678 (1906); *ibid.*, **45**, 121 (1912), etc. For a full list of references, see Weinland, "Komplexverbindungen," Ferd. Enke, Stuttgart, 1924.