occurs at about the same temperature as for the rubber by itself while the high temperature peak is nearly the same as for pure polystyrene.[7] In such mixtures the rubbery component has very little plasticizing action on the higher "melting" component.

Conclusions

Dynamic mechanical tests are a promising new tool in the study of high polymeric substances for freedom of molecular motion, solubility and molecular aggregation, and chemical heterogeneity. Such measurements, especially the damping, give very sensitive indications of the environment in which the molecular segments find themselves. In this respect the tests are similar to tests of

dielectric constant and power factor[13,14] but have the added advantage that they apply to non-polar materials as well as polar ones.

Acknowledgments.—The assistance of Robert Pollard and others on the preparation of the various copolymers was greatly appreciated. The β-cyanoethoxyethyl acrylate copolymers were made by Richard Morner. Leland Child made the viscosity determinations, and Stephania Jaworska made the chlorine analyses. The many discussions with Rolf Buchdahl during the course of this work have been of much assistance.

(13) R. Fuoss. THIS JOURNAL. **61**, 2334 (1939): **63**. 2401. 2410. 2832 (1941).

(14) A. Schallamach. *Trans. Faraday Soc.*. **45**. 605 (1949).

SPRINGFIELD, MASS.

Mechanism of Initiation of Emulsion Polymerization by Persulfate[1]

BY I. M. KOLTHOFF, E. J. MEEHAN AND E. M. CARR

The rate of disappearance of potassium persulfate has been determined in aqueous solutions containing methanol, ethanol or allyl alcohol in the absence and presence of allyl acetate. Allyl acetate does not affect the initial rate of disappearance of persulfate. Methanol and ethanol cause pronounced increases in the rate. but in the presence of allyl acetate and methanol or ethanol the rate is about the same as in the presence of allyl acetate alone. The results are interpreted on the assumption that persulfate does not react directly with any of the above organic substances but that sulfate free radicals are produced only by thermal dissociation of persulfate. In the absence of allyl acetate the sulfate radical reacts with methanol or ethanol forming a free radical derived from the alcohol. This in turn reacts with persulfate forming another sulfate radical thus leading to chain decomposition of persulfate. In the presence of both allyl acetate and alcohol essentially all the sulfate radicals are captured by allyl acetate and the chain decomposition is prevented.

Introduction

The mechanism of initiation of emulsion polymerization by persulfate is not understood completely. In this paper the question is considered whether the rate of production of sulfate radicals is determined solely by the rate of thermal dissociation of persulfate[2]

$$S_2O_8^{--} \longrightarrow 2SO_4^{-}\cdot \qquad (1a)$$
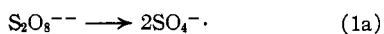
or whether persulfate also reacts directly with monomer M

$$S_2O_8^{--} + M \longrightarrow {}^-SO_4M\cdot + SO_4^{-}\cdot \qquad (2)$$
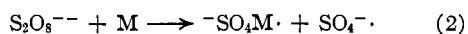
The reaction between persulfate and allyl acetate has been studied in the absence and presence of simple alcohols. The kinetics of the reaction of persulfate with methanol has been investigated previously by Bartlett and Cotman.[3] The results did not show conclusively whether the primary step was thermal dissociation (reaction 1a) or reaction (1b)

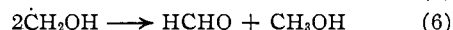$$S_2O_8^{--} + CH_3OH \longrightarrow SO_4^{-}\cdot + HSO_4^{-} + \dot{C}H_2OH \quad (1b)$$
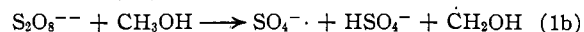
According to Bartlett and Cotman[3] the further sequence of reactions is represented by the equations (numbering of equations corresponds to that of Bartlett and Cotman)

$$SO_4^{-}\cdot + CH_3OH \longrightarrow HSO_4^{-} + \dot{C}H_2OH \quad (4)$$
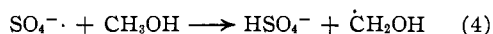
(1) The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation. Office of Synthetic Rubber. in connection with the Government Synthetic Rubber Program.

(2) I. M. Kolthoff and I. K. Miller. THIS JOURNAL. **73**. 3055 (1951).

(3) P. D. Bartlett and J. Cotman. Jr.. *ibid.*. **71**. 1419 (1949).

$$\dot{C}H_2OH + S_2O_8^{--} \longrightarrow HCHO + HSO_4^{-} + SO_4^{-}\cdot \quad (5)$$

$$2\dot{C}H_2OH \longrightarrow HCHO + CH_3OH \qquad (6)$$

In this paper it has been found that the sulfate radical adds to allyl acetate more quickly than it reacts with an alcohol. From the results it is inferred that the chain reaction between persulfate and alcohols is initiated by sulfate radicals formed in the thermal dissociation of persulfate and not by direct reaction between persulfate and alcohol. Similarly the polymerization of allyl acetate is initiated by sulfate radicals formed by thermal dissociation and not by reaction 2.

Experimental

Materials.—The following liquids were purified by distillation at atmospheric pressure using a 12-inch column packed with glass helices. Allyl acetate: Eastman Kodak Co., b.p. 101–102°; the distillate was acid-free; it was stored in a refrigerator until used. Allyl alcohol: Eastman Kodak Co., b.p. 94–96°; bromometric titration indicated a purity of 99.6%. Ethanol: absolute, commercial grade. Methanol: Baker reagent. Potassium persulfate: Merck analytical reagent, recrystallized; 99.5% pure according to iodometric titration.[4] All other materials were reagent grade chemicals.

Analytical Methods.—In most of the work persulfate was determined by the ferrous iron method in the presence of a large concentration of sodium bromide. A complete description of the determination of persulfate in the presence of organic compounds is to appear elsewhere.[4] Formaldehyde was determined by use of the color reaction with chromotropic acid.[5] Allyl acetate was determined bromometrically.

(4) I. M. Kolthoff and E. M. Carr. *Anal. Chem.*. **25**, (1953). in press.

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

Procedure.—All the experiments were performed in the absence of oxygen at 70 ± 0.5° or at 60 ± 0.5° depending on the rate of the reaction being studied. A phosphate buffer was used of the composition (in the reaction mixture): ($H_2PO_4^-$), 0.050 M; (HPO_4^{--}), 0.072 M; ionic strength 0.27, pH 6.9 (room temperature). It was necessary to work in neutral or slightly acid medium in order to prevent the hydrolysis of allyl acetate, which occurs relatively rapidly at 70° in even slightly alkaline solution. The rate of hydrolysis at 70° at pH 9 (borax buffer) was determined by titration of the total acid (acetic acid plus boric acid) present after various times. Titration with 0.1 N sodium hydroxide to a phenolphthalein end-point in the presence of mannitol, with correction for the boric acid present initially in 0.05 M borax, gave the amount of acetic acid within about 1% when the concentration was about 0.05–0.1 M. In this way it was found that allyl acetate present at initial concentration of 0.1 M hydrolyzed at pH 9 to the extent of 50% in 1.2 hours, 60% in 2.0 hours, and more than 86% in 25.8 hours at 70°. In neutral (pH 7) or slightly acid medium (pH 5) hydrolysis was negligible during the time of the experiments. In a phosphate buffer of pH 6.2 and in an acetate buffer of pH 5.5 only 1–2% hydrolysis occurred in 6 hours at 80°.

All the constituents with the exception of persulfate were placed in a volumetric flask and nitrogen was passed through the solution for at least 20 minutes. Separate experiments showed that no change in composition occurred during this operation. The flask was stoppered and placed in the thermostat. After thermal equilibrium was reached, the stopper was removed while a stream of nitrogen was directed over the neck of the flask; solid potassium persulfate was added and the stopper was replaced quickly. The solid dissolved in less than five minutes. Aliquot samples were removed at various times, entrance of oxygen during the sampling being prevented as mentioned above.

Results

The first order decomposition of persulfate at 70° in the absence of organic substances is shown in Fig. 1, curve 1. The rate constant is 0.087
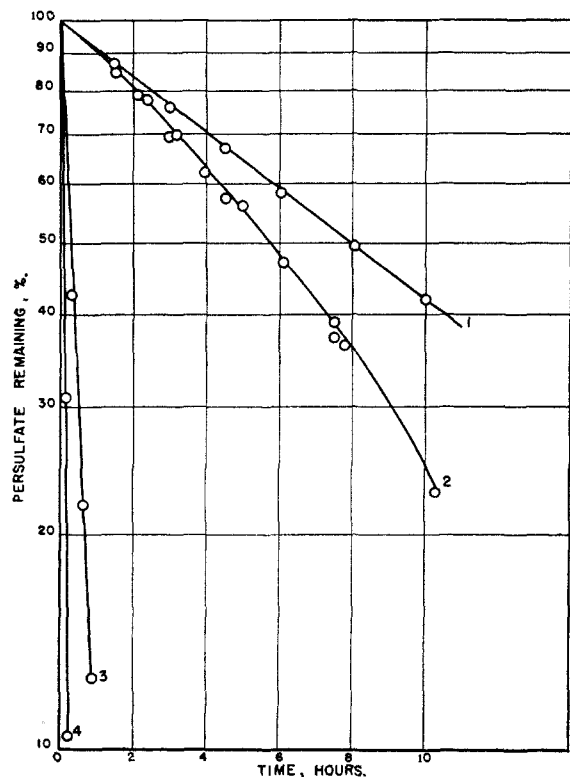

Fig. 1.—Disappearance of persulfate at 70°, pH 6.9; initial concentration of persulfate, 0.01 M: curve 1, no organic substances; curve 2, 0.024–0.17 M allyl acetate; curve 3, 0.1 M methanol; curve 4, 0.1 M ethanol.

hour^{-1} (half-time 8.0 hours) in good agreement with the value reported earlier.[2] In the presence of 0.024–0.17 M allyl acetate the apparent decomposition is not first-order (curve 2). In separate experiments polyallyl acetate was found to react slowly with persulfate and the deviation from first order decomposition is attributed to this reaction. The initial rate of decomposition is the same as that observed in the absence of allyl acetate, and the rate is unchanged when the concentration of allyl acetate is varied eightfold (half-time, 5.7–5.9 hours). These facts show conclusively that persulfate does not react directly with allyl acetate.

In the presence of 0.1 M methanol or 0.1 M ethanol the half-time at 70° is reduced to 0.33 hour or 0.1 hour, respectively. Data obtained at 60° in the presence of 0.971 M or 0.242 M methanol are plotted in Fig. 2, the ordinate being $(S_2O_8^{--})^{-1/2}$. The data obtained after an initial reaction period of 20 minutes fall on a straight line indicating a $^3/_2$-order reaction, in good agreement with the result of Bartlett and Cotman.[3] However during the first 20 minutes the experimental points do not fall on the straight line: this was also observed but not further considered by Bartlett and Cotman (see Fig. 2 of ref. 3). It appears on the basis of the results described below that this initial deviation from $^3/_2$-order may be significant. The slopes of the curves corresponding to fourfold variation in concentration of methanol differ by 1.8-fold, confirming the statement[3] that the rate is approximately proportional to the square root of the concentration of methanol.
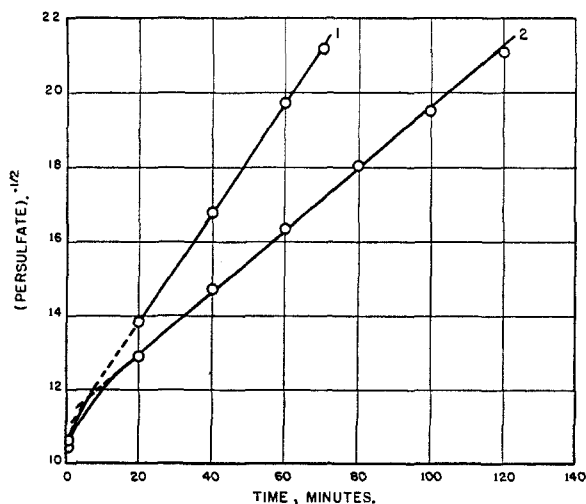

Fig. 2.—Disappearance of persulfate at 60°, pH 6.9: initial concentration of persulfate, 0.01 M: curve 1, 0.971 M methanol; curve 2, 0.242 M methanol.

The disappearance of persulfate at 60° in the presence of both allyl acetate and methanol is shown in Fig. 3, curve 3. The rate of disappearance is practically equal to that in the presence of allyl acetate alone (curve 1), and the pronounced acceleration due to methanol alone (curve 2) is virtually eliminated.

The amount of formaldehyde formed in the absence of allyl acetate was determined during the

course of the reaction and compared with the amount of persulfate decomposed. At all stages of the reaction about 80% of the stoichiometric amount (1:1 mole ratio) of formaldehyde was found, formic acid probably being the other reaction product. In the presence of 0.1 M allyl acetate and methanol no formaldehyde was detected after 16 hours at 60°.

Experiments similar to those described above have been done with ethyl alcohol and allyl alcohol. The experimental details are found elsewhere.[6] Both alcohols accelerate the decomposition of persulfate and the addition of allyl acetate suppresses the effect. At equimolar concentrations of alcohol a given concentration of allyl acetate suppresses the reaction of the alcohol with persulfate in the order allyl alcohol (least), ethanol and methanol (greatest suppression).

Discussion

From the fact that allyl acetate does not affect the rate of decomposition of persulfate (except for a slight side reaction discussed above) it follows that all the free radicals which initiate the polymerization of allyl acetate are formed by thermal dissociation of persulfate according to reaction (1a). Since the relatively rapid decomposition of persulfate in the presence of alcohols is reduced practically to the rate of thermal decomposition in the additional presence of allyl acetate, it is clear that: (1) alcohol does not react directly with persulfate by reaction (1b), and (2) allyl acetate is an efficient captor of SO_4^-· free radicals. Reaction (4) must be much slower than reaction (2), in which M denotes allyl acetate, and the chain decomposition of persulfate by alcohols (reactions 4 and 5) is practically eliminated in the presence of allyl acetate.

It should be pointed out that the kinetics of disappearance of persulfate in the presence of methanol do not correspond to the sequence 1a–4–5–6. According to this sequence the rate of disappearance should be[3]

$$d(S_2O_8^{--})/dt = k_{1a}(S_2O_8^{--}) + k_5\sqrt{k_{1a}/k_6}(S_2O_8^{--})^{3/2} \quad (1)$$

in which the first term is negligible compared to the second term (provided that the concentration of methanol is large enough). The sequence does not account for the dependence of the rate of disappearance on the square root of the concentration of methanol. In the alternate sequence suggested by Bartlett and Cotman,[3] 1b–4–5–6, the rate should be:

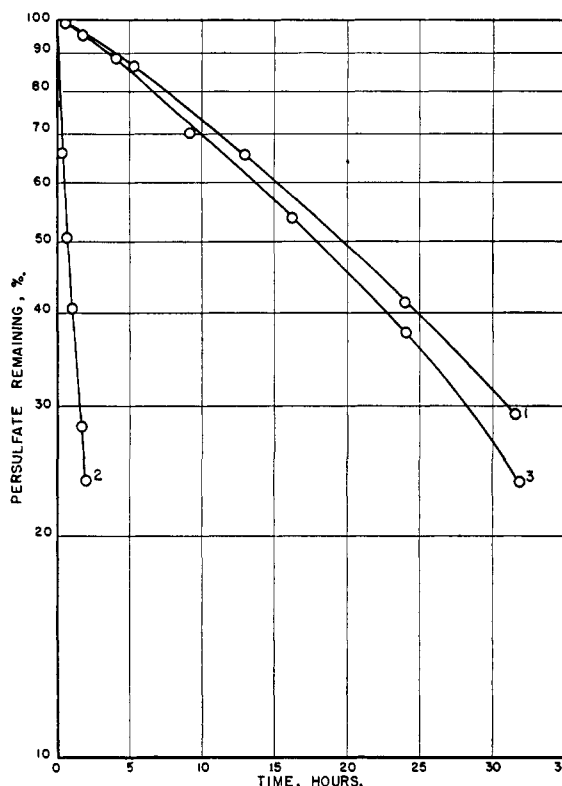(6) E. M. Carr, M.S. Thesis, University of Minnesota, 1952.

Fig. 3.—Disappearance of persulfate at 60°, pH 6.9; initial concentration of persulfate 0.01 M: curve 1, 0.10 M allyl acetate; curve 2, 0.243 M methanol; curve 3, 0.10 M allyl acetate, 0.243 M methanol.

$$-d(S_2O_8^{--})/dt = k_{1b}(S_2O_8^{--})(CH_3OH) + k_5\sqrt{k_{1b}/k_6}(S_2O_8^{--})^{3/2}(CH_3OH)^{1/2} \quad (2)$$

If the first term on the right were negligible, this sequence would predict the correct dependence of the rate on concentration of persulfate and methanol. However this term cannot be neglected compared to the second term, for if it were negligible it would be no more important than the first term on the right of equation (1). The sequence 1b–4–5–6 actually predicts a complex order in both persulfate and methanol, and in any case is invalidated by the results of this paper. Thus the apparent square-root dependence on concentration of methanol remains unexplained.

It appears probable that products of the reaction may play important roles in determining the kinetics. Experiments now being made in this Laboratory have shown that both formaldehyde and formic acid (or formate ion) exert marked accelerating affects on the decomposition of persulfate.

MINNEAPOLIS, MINNESOTA