

# Mechanism of Persulfate Decomposition in Aqueous Solution at 50°C in the Presence of Vinyl Acetate and Nitrogen

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## Synopsis

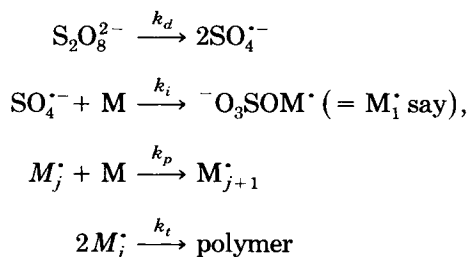
The rate of the thermal decomposition of potassium persulfate has been studied in an unbuffered aqueous solution at 50°C in nitrogen atmosphere in the presence of vinyl acetate (VA) monomer (M). It has been found that the initial rate of persulfate decomposition may be written as

$$-d(\text{S}_2\text{O}_8^{2-})/dt \propto (\text{S}_2\text{O}_8^{2-})^{1.49 \pm 0.05} \times (M)^{0.50 \pm 0.06}$$

in the concentration range of persulfate ( $1.85 \times 10^{-2}$ – $1.85 \times 10^{-3}$  m/dm<sup>3</sup>) and VA (0.054–0.27 m/dm<sup>3</sup>). The pH of the aqueous solution of persulfate was found to decrease continuously at 50°C, but there was no measurable change of pH of the aqueous solution containing persulfate and VA at 50°C in the presence of nitrogen at the early stages of the reaction. VA, methyl acetate, and ethyl acetate have been found to undergo very slow hydrolysis in aqueous solution at 50°C. The partition coefficient ( $\beta$ ) of the monomer between the polymer phase and the aqueous phase was found to be  $21 \pm 2$  in the presence and absence of electrolytes ( $\text{K}_2\text{SO}_4$ ,  $10^{-4}$ – $10^{-3}$  m/dm<sup>3</sup>) by the bromometric estimation of the monomer present in the aqueous phase containing known amounts of monomer [1.80–2.20%, w/v] and freshly prepared polymer (0.3–0.5 g/100 mL). Above  $10^{-2}$  (m/dm<sup>3</sup>) persulfate, the polymer obtained was found to be insoluble in common solvents, viz., acetone, benzene, etc. Highly purified sodium dodecyl sulfate ( $0.5$ – $5.0 \times 10^{-3}$  m/dm<sup>3</sup>) had no measurable effect on the rate of persulfate decomposition.

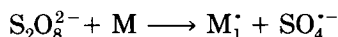
## INTRODUCTION

It is generally believed<sup>1-5</sup> that the persulfate ion in aqueous solutions dissociates thermally into two  $\text{SO}_4^{\cdot-}$  ion free radicals (originally postulated by Baxendale and Evans<sup>6</sup>) as a first step in the thermal decomposition of persulfate ions. In the presence of vinyl monomers and nitrogen, these free radicals initiate polymerization of vinyl monomers,<sup>4,5</sup> viz.,



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Such a mechanism predicts that the rate of persulfate decomposition would be first order in persulfate and independent of monomer concentrations, which is open to experimental verification. Recently it has been suggested that vinyl monomers,<sup>7</sup> detergents,<sup>7-9</sup> and latex particles<sup>8</sup> accelerate the thermal decomposition of persulfate ions in aqueous solutions, and they have suggested<sup>7</sup> that  $k_d$  is a function of the nature of the monomer, its concentration in the aqueous phase, and increases with the increase of monomer concentrations. Dunn,<sup>10a</sup> Litt et al.,<sup>11</sup> and Chang<sup>12</sup> have suggested that the accelerated rate of persulfate decompositions in the emulsion polymerization of vinyl acetate is due to the oxidation of water soluble monomeric radicals by the  $S_2O_8^{2-}$  ions. Further, Dunn has stated<sup>10a</sup> that "no evidence was found for any large enhancement of the initiation rate by persulfate due to the presence of additives as was implied by the results reported by Morris and Parts."<sup>7</sup> We have recently reported<sup>13,14</sup> the mechanism of persulfate decomposition in the presence of ethylacrylate<sup>13</sup> and of acrylonitrile<sup>14</sup> and have found that  $k_d$  does not alter in the presence of these two monomers, but the following reactions are also important:



and



where  $(M_j^{\cdot})_w$  is a water-soluble oligomeric or polymeric free radicals. We are reporting here the results of persulfate decomposition in the presence of vinyl acetate and nitrogen at 50°C in an unbuffered aqueous solution of the monomer containing persulfate.

## EXPERIMENTAL

Quality of chemicals used and their purifications have been described elsewhere in detail.<sup>13,14</sup> The reactions have been carried out in four-necked Pyrex 1-L round-bottom flask fitted with a Hg-seal stirrer, an arrangement for nitrogen passing into the solution, and sampling devices in the presence of nitrogen.<sup>15</sup> Undecomposed persulfate was estimated by the methods of Kolthoff and Carr,<sup>16</sup> while polymerizations of VA were followed gravimetrically.<sup>15</sup> Vinyl acetate (S.D.'s fine chem. of Bombay, India, and Kochlight, U.K. grade) was distilled in vacuum. The distillate was refluxed with 0.05% (w/v) benzoyl peroxide in the presence of nitrogen. As soon as the mixture became viscous, it was vacuum distilled and fractionated into three parts. The middle fraction (refractive index 1.3954 at 20°C) was used for polymerization and for persulfate decomposition,<sup>17,18</sup> and stored at 0–5°C in a refrigerator. Before use, the monomer was tested for peroxide. If peroxide was detected, it was refluxed in the presence of nitrogen, vacuum distilled, and used. pH of the solutions was measured at 25°C, and the molecular weights of the polymers were estimated viscometrically in acetone solvent, while the colloidal stability of the latex solution was estimated by titrating with a standard [(N/20) to (N/100)]  $MgSO_4$  solution.<sup>19,20</sup> Sodium dodecyl sulfate (Kochlight, UK, grade

or of Loba Chemie Co. Bombay, India, grade) was purified by the method of Dunn et al.<sup>21a</sup> and of Harrold.<sup>21b</sup>

### RESULTS

The results of persulfate decomposition in the presence of VA are shown in Figures 1-5 and Tables I-III. Figure 1 shows the undecomposed persulfate as a function of time at various concentrations of the monomer at 50°C. From the data of Figure 1, it is evident that the rate of persulfate decomposition is a function of the monomer concentrations in the aqueous phase, and the rate increases with the increase of monomer concentrations. It also shows that the purified soap, sodium dodecyl sulfate, had no measurable effect on the rates of persulfate decomposition.

Figure 2 shows the time average rates of persulfate decomposition as a function of time at a given concentration of the monomer (VA) and at various concentrations of the initiator. It is clear from Figure 2 that the time average rates of persulfate decomposition decreased with time or with the conversion

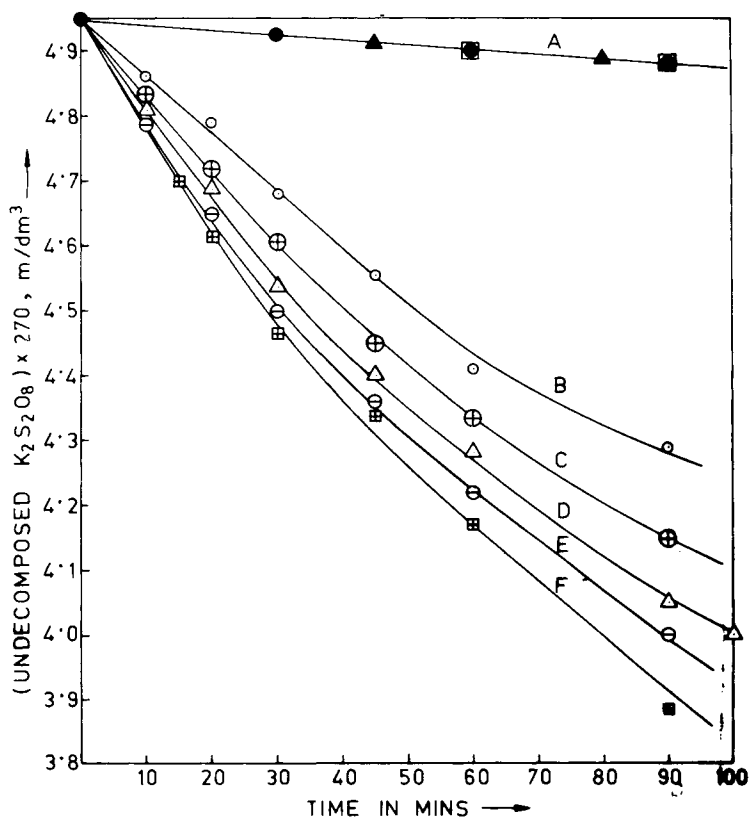


Fig. 1. The effect of vinyl acetate (VA), of poly(vinyl acetate) (PVA) and of sodium dodecyl sulfate (SDS) on the rates of thermal decomposition of  $K_2S_2O_8$  ( $1.83 \times 10^{-2}$  m/dm<sup>3</sup>) at 50°C in aqueous solution in nitrogen atmosphere. Curve A shows the effects of PVA and of SDS on persulfate decomposition. (●) persulfate alone; (▲) in the presence of SDS ( $5.0 \times 10^{-3}$  m/dm<sup>3</sup>); and (□) in the presence of PVA ( $3 \times 10^{-3}$  kg/dm<sup>3</sup>). Curves B-F show the effects of VA; (B) with 0.054; (C) with 0.1086; (D) with 0.163; (E) with 0.217; (F) with 0.2715 m/dm<sup>3</sup> VA.

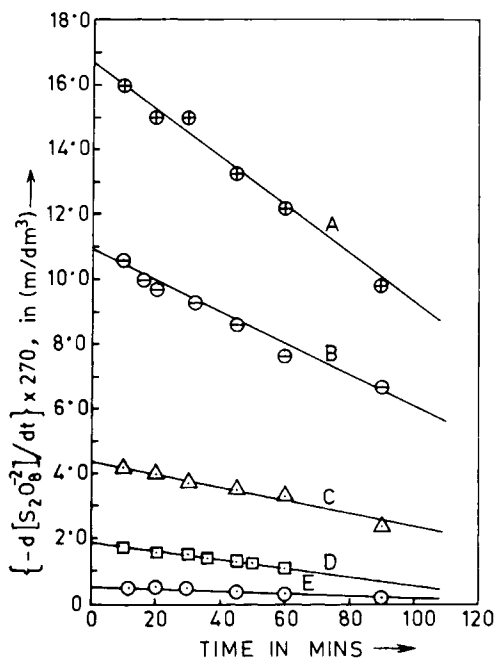


Fig. 2. The determination of initial rates of persulfate decomposition at various concentrations of  $K_2S_2O_8$  at a given concentration of VA ( $0.217 \text{ m/dm}^3$ ): (A) with  $1.83 \times 10^{-2}$ ; (B)  $1.48 \times 10^{-2}$ ; (C)  $0.926 \times 10^{-2}$ ; (D)  $0.463 \times 10^{-2}$ ; (E)  $0.185 \times 10^{-2} \text{ m/dm}^3 K_2S_2O_8$ .

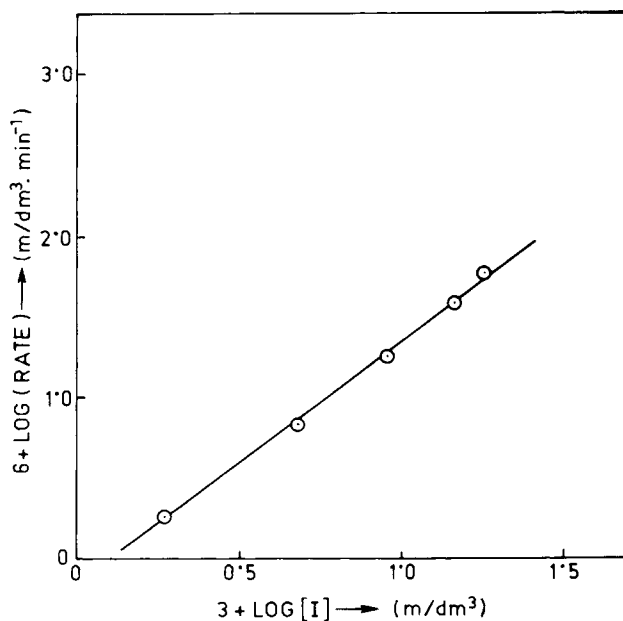


Fig. 3. The conventional order plot of the initiator. Slope of the line (log rate vs. log concn of the initiator) was found to be 1.49.

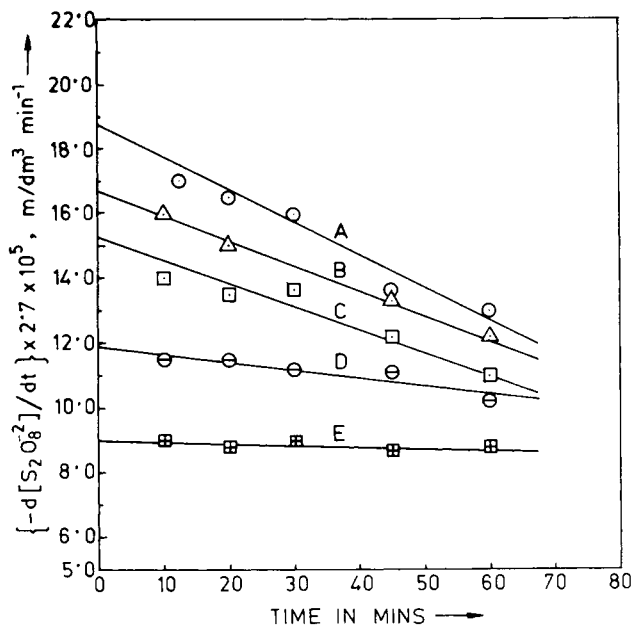


Fig. 4(a). The determination of the initial rates of persulfate decomposition at various concentrations ( $\text{m/dm}^3$ ) of VA and at a given concentration of  $\text{K}_2\text{S}_2\text{O}_8$  ( $1.83 \times 10^{-2} \text{ m/dm}^3$ ): (A) 0.2715; (B) 0.217; (C) 0.163; (D) 0.1086; (E) 0.054. The intercept at zero time is assumed to be the initial rate under a given condition.

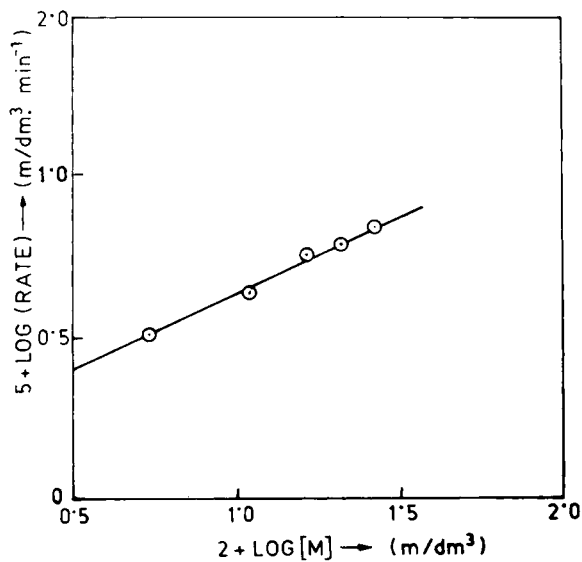


Fig. 4(b). The conventional order plot for monomer. The slope of the line was about 0.50.

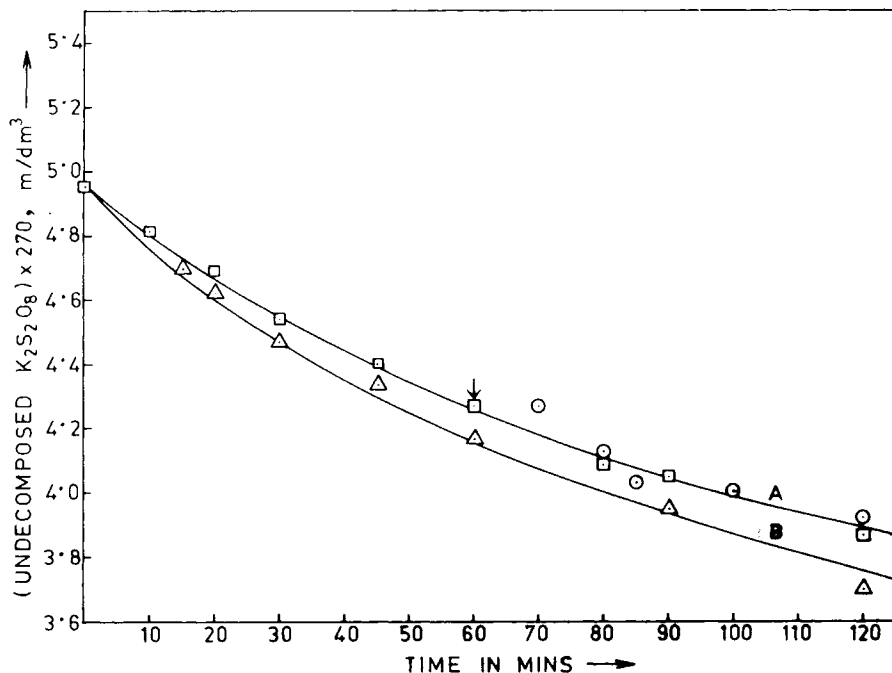


Fig. 5. The undecomposed persulfate as a function of time at two different concentrations of VA, and also the effect of VA injected late in a run, on persulfate decomposition: (A)  $K_2S_2O_8$   $1.83 \times 10^{-2}$   $m/dm^3$ , VA  $0.163$   $m/dm^3$ ; (B)  $K_2S_2O_8$   $1.83 \times 10^{-2}$   $m/dm^3$ , VA  $0.2715$   $m/dm^3$ . In curve A, an additional quantity of monomer ( $0.1086$   $m/dm^3$ ) was injected after about 78% conversion of monomer to polymer. The arrow in the figure indicates the time of injection of monomer in duplicate runs. ( $\square$ ) corresponds to the control run of A, while ( $\circ$ ) corresponds to the injected system.

of monomer to polymer in a given run, approximately linearly at the early stages of the reaction. The initial rate of decomposition of persulfate at zero time in a given run, is determined by extrapolating the linear curves of Figure 2 to zero time.

Figure 3 shows the conventional order plot for the initiator, in which  $\log(\text{initial rate})$  vs.  $\log(\text{initiator})$  has been plotted. The slope of the line, about 1.50, gives the order of the initiator with respect to persulfate decomposition.

Figure 4(a) shows the estimation of initial rates of persulfate decomposition from the data of Figure 1 at various concentrations of the monomer and at a given concentration of persulfate. Figure 4(b) shows the conventional order plot of the monomer, found to be  $0.50 \pm 0.06$ . Figure 5 shows the effect of monomer on the rates of persulfate decomposition, when injected late in a run (after 75–80% conversion of the initial monomer to polymer). It is found that the injected monomer had no measurable effect on the rate of persulfate decomposition.

Table I shows the pH variation (measured at  $25^\circ C$ ) as a function of reaction time. The pH of the solution containing 2.5% (v/v) VA, and  $10^{-3}$  ( $m/dm^3$ )  $K_2S_2O_8$  did not alter with time up to 60% conversion of monomer to polymer at  $50^\circ C$ , to a significant extent. It appears that an aqueous solution of VA, methyl acetate or ethyl acetate undergoes slow hydrolysis at  $50^\circ C$  in nitrogen

TABLE I  
Variation of pH of the Aqueous Solutions Containing Various Amounts of Monomer and Initiator at 50°C, pH Measured at 25°C

Composition of solutions <sup>a</sup>	Time (min)						
	0	10	15	20	30	45	60
A	pH → 4.55	4.55	4.55	4.50	4.55	4.50	4.45
	% Polymerized →	0.00	3.50	7.50	20.0	62.0	81.5
B	pH 5.50	—	—	—	5.30	—	5.10
C	pH 4.60	4.60	—	—	4.50	4.45	4.40
D	pH 6.40	6.40	—	—	6.15	6.00	5.90
E	pH 6.50	6.50	—	6.40	—	6.20	6.00

<sup>a</sup>A = 2.5% (v/v) VA + 10<sup>-3</sup> (m/dm<sup>3</sup>) K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, B = 10<sup>-3</sup> (m/dm<sup>3</sup>) K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, C = 2.5% (v/v) VA, all in N<sub>2</sub> atmosphere at 50°C, D = 2.0% (v/v) methyl acetate, and E = 2.0% (v/v) ethyl acetate. The total volume of each solution for pH measurement was 100 mL.

atmosphere, while the pH of the aqueous persulfate solution (10<sup>-3</sup> m/dm<sup>3</sup>) at 50°C in nitrogen atmosphere decreased slowly with time. The partition coefficient ( $\beta$ ) of the monomer between the polymer and the aqueous phases at 50°C in nitrogen atmosphere has been estimated by the bromometric estimation of the monomer present in the aqueous phase containing known amount of monomer (1.8–2.2% w/v) and of polymer (0.3–0.5 g/100 mL) in the presence and absence of electrolytes (K<sub>2</sub>SO<sub>4</sub>: 10<sup>-4</sup>–10<sup>-3</sup> m/dm<sup>3</sup>). The mixture was kept for 8 h at 50°C in N<sub>2</sub> atmosphere for equilibration. The value of ( $\beta$ ) was found to be 21 ± 2. This agrees well with the data of Taylor<sup>22</sup> at relatively higher initial concentration of monomer in the aqueous phase. In the initial concentration range of monomer from 0.56 to 2.99 g/100 mL of latex solution, Taylor found that  $[M]_p/[M]_w$  was not constant, but  $[M]_p^{1/2}/[M]_w$  was approximately constant.

The data of Table I show clearly that there is no significant pH change up to 20% conversion of monomer to polymer. Comparing the results of pH

TABLE II  
pH of Aqueous Solutions Containing K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and VA

Composition of solution in air at 50°C	pH measured at 25°C		Observation
	At zero time	After 1 h of reaction	
(1) 2.5% (v/v) VA in distilled water (pH 7)	4.60	4.40	No polymer
(2) 0.1 (m/dm <sup>3</sup> ) K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3.15	2.95	—
(3) 0.1 (m/dm <sup>3</sup> ) K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + 2.5% (v/v) VA (total volume 0.1 dm <sup>3</sup> )	3.15	2.75	62% polymer formed, but insoluble in acetone.
(4) 0.1 (m/dm <sup>3</sup> ) K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + 0.5% (v/v) VA; (total volume 0.1 dm <sup>3</sup> )	3.15	2.95	No polymer

TABLE III  
 Polymerization of VA in Aqueous Solution in N<sub>2</sub> atmosphere at 50°C<sup>a</sup>

K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (m/dm <sup>3</sup> )	10 <sup>-3</sup>	10 <sup>-2</sup>	5 × 10 <sup>-2</sup>	10 <sup>-1</sup>
% Polymer in 1 h	40.0	60.0	38.0	No polymer but persulfate decomposition was about (23 ± 0.5)%, average of five experiments; smell of VA disappeared
Solubility in acetone	Soluble in acetone	a <sup>b</sup>	a <sup>b</sup>	—
$\bar{M}_n \times 10^{-5}$ from viscosity measurement.	3.2	—	—	—
With 0.2715 (m/dm <sup>3</sup> ) VA and various concn of persulfate, and time 1 h for polymerization	88% polymer	95% polymer	—	62% polymer
Solubility in acetone	Soluble in acetone	a <sup>b</sup>	—	a <sup>b</sup>
$\bar{M}_n \times 10^{-5}$	3.8	—	—	—

<sup>a</sup> Persulfate varies, and VA, 0.054 m/dm<sup>3</sup>.

<sup>b</sup> a = the polymer swelled in acetone but did not dissolve within a week.

change with time, it seems that VA hydrolysis is faster than methyl acetate or ethyl acetate hydrolysis in aqueous solutions under identical experimental conditions. The data of Table II shows that the reactions became very complex at higher concentrations of the initiator. It appears that the polymer molecules are attacked by the persulfate ions leading to crosslinked polymer which is insoluble in acetone. The data of Table III also support this observation. Incidentally we would like to point out that we found the pH of a freshly prepared 0.1 (m/dm<sup>3</sup>) VA solution containing 8.0 × 10<sup>-4</sup> (m/dm<sup>3</sup>) K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as 5.25 at 25°C, whereas Dunn and Chong,<sup>10b</sup> reported pH as 3.35. The pH of a freshly prepared 8.0 × 10<sup>-4</sup> (m/dm<sup>3</sup>) K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution was 6.20 and that of 0.1 (m/dm<sup>3</sup>) VA solution in distilled water (pH 6.95) was 5.30. We recrystallized the potassium persulfate (GR grade of E. Merck, India) three times from double distilled water.

## DISCUSSION

Experimental results presented here show clearly that the initial rate of persulfate decomposition in an unbuffered aqueous solution (pH 3–7) may be written as (ionic strength was kept constant by adding K<sub>2</sub>SO<sub>4</sub>):

$$-d(\text{S}_2\text{O}_8^{2-})/dt \propto (\text{M})^{0.50 \pm 0.06} \times (\text{S}_2\text{O}_8^{2-})^{1.49 \pm 0.05}$$

This fact cannot be explained by the conventional mechanism as stated in the introduction. The following reactions are found to give a satisfactory quantitative description of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions decomposition in aqueous solutions in the



presence of VA:

- (1)  $S_2O_8^{2-} \xrightleftharpoons[k_{-1}]{k_1} (2SO_4^{\cdot-})_{\text{cage}}$
- (2)  $(2SO_4^{\cdot-})_{\text{cage}} \xrightarrow{k_D} SO_4^{\cdot-} + SO_4^{\cdot-}$  (diffusing out into the bulk phase)
- (3)  $(2SO_4^{\cdot-})_{\text{cage}} + M \longrightarrow M_1^{\cdot} (= ^-O_3SOM^{\cdot}) + SO_4^{\cdot-}$
- (3a)  $(2SO_4^{\cdot-})_{\text{cage}} + M \longrightarrow HSO_4^- + R^{\cdot} + SO_4^{\cdot-}$
- (4)  $SO_4^{\cdot-} + M \longrightarrow M_1^{\cdot}$ , in the aqueous phase
- (4a)  $SO_4^{\cdot-} + M (= RH) \longrightarrow HSO_4^- + R^{\cdot}$ , in the aqueous phase
- (5)  $S_2O_8^{2-} + M \longrightarrow M_1^{\cdot} + SO_4^{\cdot-}$ , in the aqueous phase
- (5a)  $S_2O_8^{2-} + RH \longrightarrow HSO_4^- + R^{\cdot} + SO_4^{\cdot-}$ , in the aqueous phase
- (6)  $M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$
- (7)  $M_j^{\cdot} + M \xrightarrow{k_p} M_{j+1}^{\cdot}$
- (8)  $M_j^{\cdot} + RH \xrightarrow{k_{tr,m}} M_jH + R^{\cdot}$
- (9)  $(M_j^{\cdot})_w + S_2O_8^{2-} \longrightarrow M_j-O-SO_3^- + SO_4^{\cdot-}$ , in the aqueous phase
- (10)  $(M_j^{\cdot})_w \rightleftharpoons (M_j^{\cdot})_p$ , at the particle-water interface
- (11)  $(M)_w \rightleftharpoons (M)_p$ , at the particle-water interface
- (12)  $(M_j)_w + P$  (dead particle)  $\rightleftharpoons P^*$  (active particle)
- (13)  $2(M_j^{\cdot})_w \xrightarrow{k_{tw}} \text{polymer}$ , in the aqueous phase
- (14)  $2(M_j^{\cdot})_p \xrightarrow{k_{tp}} \text{polymer}$ , in the latex particles
- (15)  $R^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$
- (16)  $(2SO_4^{\cdot-})_{\text{cage}} + H_2O \longrightarrow HSO_4^- + SO_4^{\cdot-} + OH$
- (17)  $SO_4^{\cdot-} + H_2O \longrightarrow HSO_4^- + OH$
- (18)  $OH + M \longrightarrow HO-M^{\cdot} (= M_1^{\cdot})$
- (19)  $2OH \longrightarrow H_2O + (1/2)O_2$ , or  $H_2O_2$

According to Noyes,<sup>23</sup> primary recombination of neutral free radicals inside the solvent cage takes place within  $10^{-13}$  s after their formation, and no scavenger can compete with the primary recombination of free radicals inside the solvent cage. The secondary recombination of free radicals in the solvent cage takes place within  $10^{-9}$ – $10^{-11}$  s after their formation, and if the scavenger is very reactive towards the free radicals, the scavenger molecules of the solvent cage wall may then compete with the secondary recombination of free radicals. McGinniss and Kah<sup>24</sup> have correlated the reactivity of  $SO_4^{\cdot-}$  radicals with the ionization potential (IP) of vinyl monomers. Vinyl acetate (IP = 8.74, eV) reacts vigorously with the  $SO_4^{\cdot-}$  radicals, while monomers having higher IP (viz., acrylates, methacrylates, nitriles, etc.) react relatively slowly with  $SO_4^{\cdot-}$  radicals. The negatively charged  $SO_4^{\cdot-}$  radicals may repel each other inside the solvent cage, so that a fraction of them will recombine in the solvent cage by the primary and the secondary recombination processes of Noyes and the rest may react with the highly reactive scavengers of the cage wall, or diffuse out of the solvent cage into the bulk phase.

The reverse reaction of (2) seems to be highly improbable. Since the pH of the solutions did not change significantly in the presence of VA (Table I) at the early stages of the reaction and at low initiator concentrations ( $10^{-3}$  m/dm<sup>3</sup>), reactions (16), (17), and hence (18) and (19), would not be important. It is assumed that reactions (3a), 4(a), and 5(a) are not important compared to (3), (4), and (5) respectively since the pH of the solution did not change (Table I). Further, rate of (4)/rate of (17) =  $k_4(\text{SO}_4^{\cdot-})(\text{M})/k_{17}(\text{SO}_4^{\cdot-})$  is known to be very high,<sup>24,25</sup> viz., of the order of  $10^3$ – $10^4$ , and so almost all  $\text{SO}_4^{\cdot-}$  radicals would disappear via reaction (4). It seems therefore that OH radicals would not be formed in the presence of VA, and so only  $\text{SO}_4^{\cdot-}$  radicals would initiate VA polymerization. The hydroxyl end groups found in the persulfate initiated vinyl polymerization (aqueous or emulsion) could be due to the hydrolysis of sulfate end groups.<sup>5,10</sup>

Radicals  $\text{M}_i^{\cdot}$  and  $\text{R}^{\cdot}$  are assumed to be indistinguishable with respect to their chemical reactions in the system. The caged pair of radicals,  $(2\text{SO}_4^{\cdot-})_{\text{cage}}$  is treated as a single transient species, so that reactions (1), (2), and (3) are first order in these species.<sup>26</sup> It is assumed that once the primary radicals,  $\text{SO}_4^{\cdot-}$ , have diffused out of the cage, they would react only with the dissolved monomer molecules. The recombination of two nongeminate  $\text{SO}_4^{\cdot-}$  radicals is believed to be unimportant<sup>2</sup> in the presence of reactive scavengers, since the stationary concentration of  $\text{SO}_4^{\cdot-}$  radicals in the bulk phase would be very small in the presence of highly reactive scavenger, VA. The interaction between the  $\text{SO}_4^{\cdot-}$  radicals and the negatively charged latex particles (due to sulfate end groups) is believed to be unimportant.<sup>5,27</sup> Since the initiator is not soluble in the organic phase, the initiation of polymerization will be entirely in the aqueous phase. Hence the rate of initiation ( $R_i$ ) is given by

$$R_i = [2k_D(2\text{SO}_4^{\cdot-})_{\text{cage}} + 2k_3(\text{M})(2\text{SO}_4^{\cdot-})_{\text{cage}} + 2k_5(\text{I})(\text{M}) + k_9(\text{M}_j^{\cdot})_w(\text{I})] V_w \quad (1)$$

where  $(\text{M}_j^{\cdot})_w$  are water soluble oligomeric/polymeric free radicals ( $j = 1$ – $30$ , possibly<sup>10,29</sup>),  $(\text{I}) = (\text{S}_2\text{O}_8^{2-})$ , and  $V_w$  is the volume fraction of the aqueous phase. Initially the whole system was homogeneous, so  $V_w$  was unity at zero time or zero conversion of monomer to polymer. Rate of termination ( $R_{tw}$ ) in the aqueous phase is given by

$$R_{tw} = 2k_{tw}(\text{M}_j^{\cdot})_w^2 V_w \quad (2)$$

If  $V_p$  be the volume fraction of polymer, then  $V_w + V_p = 1.0$ . Assuming the contribution of the reaction (9) would be much less in the initiation reaction than the total contribution of (3), (4), and (5), we get

$$R_i = [2k_D + k_3(\text{M})(2\text{SO}_4^{\cdot-})_{\text{cage}} + 2k_5(\text{I})(\text{M})] \times V_w \quad (3)$$

Equating (2) and (3), in the steady state, we get

$$(\text{M}_j^{\cdot})_w = \left\{ \frac{[k_D + k_3(\text{M})](2\text{SO}_4^{\cdot-})_{\text{cage}} + k_5(\text{I})(\text{M})}{k_{tw}} \right\}^{1/2} \quad (4)$$

where

$$(2\text{SO}_4^{\cdot-})_{\text{cage}} = [k_1(\text{I})]/[k_{-1} + k_D + k_3(\text{M})] \cong (k_1/k_{-1})(\text{I}),$$

if  $k_{-1} > \{k_D + k_3(\text{M})\}$ . Further, if  $k_3(\text{M}) > k_D$ , we get

$$(\text{M}'_j)_w = [k_3(k_1/k_{-1}) + k_5]^{0.5}(\text{M})^{0.5}(\text{I})^{0.5}/k_{tw}^{0.5} \tag{5}$$

Hence the total rate of persulfate, (I), decomposition in the system is given by

$$-d(\text{I})/dt = k_1(\text{I}) - k_{-1}(2\text{SO}_4^{\cdot-})_{\text{cage}} + k_5(\text{M})(\text{I}) + k_9(\text{M}'_j)(\text{I}) \tag{6}$$

Reactions (1) and (-1) are independent of (M), while reactions (5) and (9) depend on (M). Equation (6) can be rearranged as

$$\begin{aligned} 1/(\text{I})[-d(\text{I})/dt] &= k_1 - [k_1k_{-1}]/[k_{-1} + k_D + k_3(\text{M})] \\ &+ k_9[(k_3K_1 + k_5)/(k_{tw})]^{1/2}(\text{M})^{1/2}(\text{I})^{1/2} + k_5(\text{M}) \end{aligned} \tag{7}$$

where  $K_1 = k_1/k_{-1}$ , if  $k_{-1} > [k_D + k_3(\text{M})]$ ; we get

$$[1/(\text{I})][-d(\text{I})/dt] = k_5(\text{M}) + k_9[(k_3K_1 + k_5)/(k_{tw})]^{1/2}(\text{M})^{1/2}(\text{I})^{1/2} \tag{8}$$

Since the experimental results show that

$$-d(\text{I})/dt \propto (\text{M})^{1/2} \times (\text{I})^{3/2}$$

it seems to us that, in this system, the reaction (5) is probably not important. Hence,

$$[1/(\text{I})][-d(\text{I})/dt] = k_9(k_3K_1/k_{tw})^{1/2}(\text{M})^{1/2}(\text{I})^{1/2} \tag{9}$$

or

$$[1/(\text{I})^{3/2}][-d(\text{I})/dt] = k_9(k_3K_1/k_{tw})^{1/2}(\text{M})^{1/2} \tag{10}$$

The plot of the lhs of eq. (9) vs.  $(\text{I})^{1/2}$  at a given concentration of the monomer (M) gives a straight line passing through the origin (Fig. 6). The slope of the line gives  $k_9(k_3K_1/k_{tw})^{1/2}(\text{M})^{1/2}$  was found as  $3.79 \times 10^{-4} (\text{dm}^3)^{1/2} \text{m}^{-1/2} \text{s}^{-1}$ . Taking  $(\text{M}) = 0.217 (\text{m}/\text{dm}^3)$ , we get  $k_9(k_3K_1/k_{tw})^{1/2}$  as  $8.314 \times 10^{-4} (\text{dm}^3 \text{m}^{-1} \text{s}^{-1})$ . At a given concentration of the initiator ( $1.85 \times 10^{-2} \text{m}/\text{dm}^3$ ), the lhs of eq. (10) is plotted against  $(\text{M})^{1/2}$ , the resulting straight line (Fig. 7) passed through the origin, the slope of which was found to be  $8.93 \times 10^{-4} (\text{dm}^3 \text{m}^{-1} \text{s}^{-1})$ . Hence the average value of  $k_9(k_3K_1/k_{tw})^{1/2}$  is  $8.54 \times 10^{-4} (\text{dm}^3 \text{m}^{-1} \text{s}^{-1})$ . Since  $k_9$ ,  $k_3$ , and  $k_{tw}$  are not known, it is not possible to estimate precisely the value of the equilibrium constant ( $K_1$ ) of the reaction (1). However, taking the approximate values of  $k_9$ ,  $k_4 (= k_3 \text{ assumed})$  and  $k_{tw}$  ( $= k_{tp}$  at zero conversion of monomer to polymer) from the literature,<sup>12,24,29</sup> we get  $K_1$  at  $50^\circ\text{C}$  about  $1.25 \times 10^{-22}$ , which indicates that the equilibrium

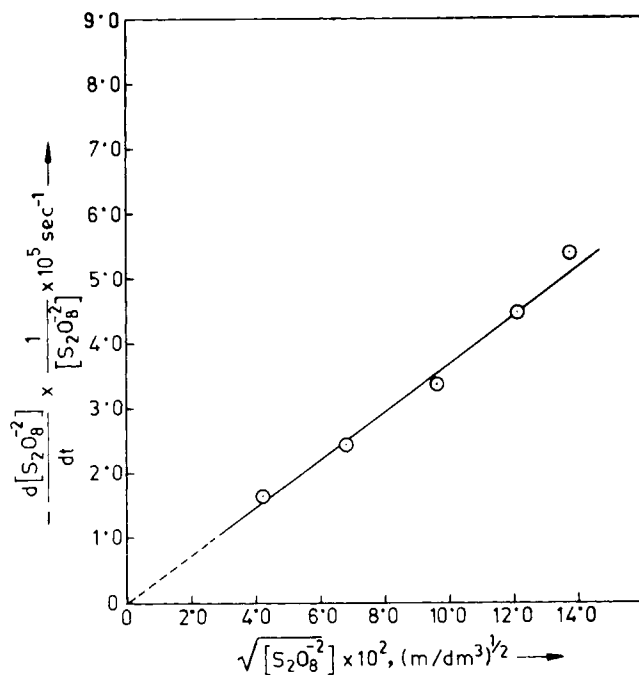


Fig. 6. The plot of  $[(S_2O_8^{2-})^{-1} \times \{-d(S_2O_8^{2-})/dt\}]$  vs.  $(S_2O_8^{2-})^{1/2}$ , according to eq. (9).

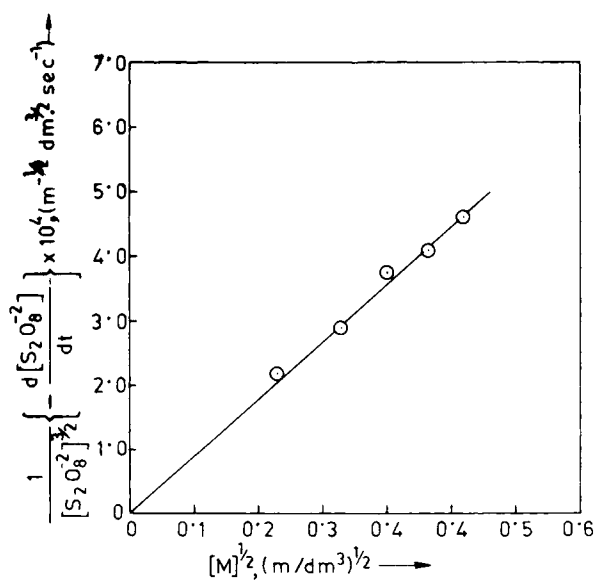
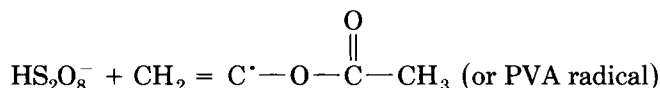
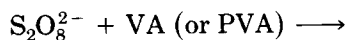


Fig. 7. The plot of  $[(S_2O_8^{2-})^{-1.5} \times \{-d(S_2O_8^{2-})/dt\}]$  vs.  $(M)^{1/2}$ , according to eq. (10).

concentration of  $(2\text{SO}_4^{\cdot-})_{\text{cage}}$  radicals is very small under the experimental conditions. Chang<sup>12</sup> gave  $k_9$  as  $2 \times 10^7$  to  $2 \times 10^8$  ( $\text{dm}^3 \text{m}^{-1} \text{s}^{-1}$ ) at  $60^\circ\text{C}$ , and we took  $k_9$  as  $2 \times 10^7$  in the same unit at  $50^\circ\text{C}$ . McGinniss and Kah<sup>24</sup> gave  $k_4$  as  $6.89 \times 10^9$  ( $\text{dm}^3 \text{m}^{-1} \text{s}^{-1}$ ), while Nomura et al.<sup>29</sup> gave  $k_{tw}$  as  $4.7 \times 10^8$  ( $\text{dm}^3 \text{m}^{-1} \text{s}^{-1}$ ).

The data of Figure 5 show clearly that the dissolved monomer molecules in the aqueous phase are interacting with the persulfate ions or sulfate ion radicals. Injected monomer late in a run (after 78% conversion of monomer to polymer) did not have any measurable effect on the rate of persulfate decomposition (Fig. 5). It seems to us that the latex particles absorbed almost all the injected monomer because of the very high distribution coefficient of the monomer, and very little of the injected monomer would remain in the aqueous phase. Brooks and Mankanjuola<sup>8</sup> also observed that VA seed latex particles (free from monomer) and monomer-swelled VA seed latex particles (monomer/polymer ratio 1.45 by weight) had accelerated the rate of persulfate decomposition by factors of 3.7 and 3.3, respectively, at  $60^\circ\text{C}$ , at about  $11.0 \times 10^{-3}$  ( $\text{m}/\text{dm}^3$ )  $\text{K}_2\text{S}_2\text{O}_8$  concentration. Similar observations were also made in the persulfate-styrene-polystyrene, and in the persulfate-methyl methacrylate-poly(methyl methacrylate) systems.<sup>8</sup>

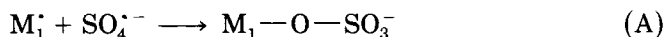
We have further observed that, at higher concentrations of persulfate (above  $5 \times 10^{-3}$   $\text{m}/\text{dm}^3$ ), the polymer (PVA) obtained is partly soluble in common solvents, viz., acetone, benzene, etc. (Tables II and III), and partly insoluble. Freshly prepared polymer (PVA) with initiator  $10^{-3}$  ( $\text{m}/\text{dm}^3$ ) and VA 0.217 ( $\text{m}/\text{dm}^3$ ), when added to persulfate solution ( $1.85 \times 10^{-2}$   $\text{m}/\text{dm}^3$ ) at  $50^\circ\text{C}$  in  $\text{N}_2$  atmosphere, did not alter the rate of persulfate decomposition within experimental error ( $\pm 3\%$ , estimated by the iodometric method of Kolthoff and Carr<sup>16</sup>) (Fig. 1). It seems to us that the crosslinked polymer was probably formed in the latex particles during polymerizations due to polymer transfer leading to crosslinked graft polymer. Brooks and Mankanjuola<sup>8</sup> did not report the solubility of PVA (present in the seed latex) in common organic solvents before and after oxidation of seed latex by the persulfate ions, nor did they report the molecular weights of PVA of seed latex. Since PVA did not alter the rates of persulfate decompositions, and the pH of the solution did not alter (Table I) during the polymerizations, we believe that the reaction



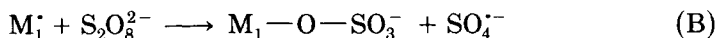
is not important at low concentrations of the initiator. Chang<sup>12</sup> has shown that the H of the C (of vinyl group) attached with the O atom of the ester is relatively more labile compared to other H atoms of the ester molecules.

We have repeated the experiment of Morris and Parts,<sup>7</sup> and have confirmed that at higher concentration of the initiator ( $0.1 \text{m}/\text{dm}^3$ ) and low monomer concentration ( $0.054 \text{m}/\text{dm}^3$ ), no polymer was formed after 1 h (Table III) of addition of the initiator to the aqueous solution of the monomer at  $50^\circ\text{C}$  in  $\text{N}_2$  atmosphere. The smell of VA disappeared as reported by Morris and Parts.<sup>7</sup> It

appears that under the experimental conditions, the following reactions become important:



and



and so no polymerization would occur. However, at higher concentrations of monomer (0.2715 m/dm<sup>3</sup>), we got polymer (62% conversion after 1 h of polymerization, Table III), which was insoluble in acetone. At higher concentration of persulfate (0.10 m/dm<sup>3</sup>), oxidation of colloidal latex particles by S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions may occur as found by Brooks and Mankanjuola<sup>8</sup> or polymer transfer reactions in the latex particles may bring about the crosslinked polymer due to chain grafting.

At higher monomer concentrations, the stationary concentration of the primary radicals (SO<sub>4</sub><sup>·-</sup>) will be smaller because of the initiation reaction (4), and so the reaction (A) would not be important. Further, under the experimental conditions, we see

$$\begin{aligned} \frac{\text{rate of (B)}}{\text{rate of propagation}} &= \frac{[k_B(M_1^{\cdot})(S_2O_8^{2-})]}{[k_p(M_1^{\cdot})(M)]} \\ &= (2 \times 10^7 \times 0.10)/(3340 \times 0.2175) = 0.275 \times 10^4 \end{aligned}$$

taking  $k_B = 2 \times 10^7$  (dm<sup>3</sup> m<sup>-1</sup> s<sup>-1</sup>) at 50°C from Chang,<sup>12</sup> and  $k_p = 3340$  (dm<sup>3</sup>/m/s) at 50°C from Nomura.<sup>30</sup> In such a case, almost all the M<sub>1</sub><sup>·</sup> radicals in the aqueous phase would be oxidized by the persulfate ions, and so no polymerization would take place. Since we got 62% polymer (Tables II and III), we believe that the rate of propagation is much higher than that of the reaction (B). It seems to us that  $k_B$  has been overestimated by Chang<sup>12</sup> from an assumed mechanism of persulfate decomposition in the presence of VA.

The suggested mechanism is probably valid for persulfate decomposition at low concentrations (10<sup>-4</sup>–10<sup>-3</sup> m/dm<sup>3</sup>), when complications due to crosslinked polymer formation would not arise. We studied the acrylonitrile–persulfate system,<sup>14</sup> and also the ethyl acrylate–persulfate system,<sup>13</sup> and got different results, viz.,

$$-d(S_2O_8^{2-})/dt \propto (AN)^{1.26}(S_2O_8^{2-})^{1.40}$$

and

$$-d(S_2O_8^{2-})/dt \propto (EA)^{1.0} \times (S_2O_8^{2-})^{1.0}$$

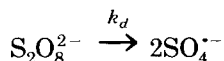
It is evident that the mechanism of persulfate decomposition in aqueous solution in the presence of vinyl monomers depends on the nature of the monomer and of the polymer formed and also on the physical state of the polymer insoluble in water. It may be pointed out here that McGinniss and

Kah<sup>24</sup> observed that SO<sub>4</sub><sup>•-</sup> radicals did not attack the anionic detergent, sodium dodecyl sulfate, and it agrees well with our results shown in Figure 1.

From Noyes' model for persulfate ion dissociation in water in the absence of scavengers, we find that

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k_1[1 - (k_{-1})/(k_{-1} + k_D)](\text{S}_2\text{O}_8^{2-})$$

neglecting the geminate and the nongeminate recombination of SO<sub>4</sub><sup>•-</sup> radicals outside the solvent cage.<sup>1-5</sup> If, however, the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ion dissociation is irreversible,<sup>2</sup> viz.,



possibly because of repulsion between the negatively charged ion radicals, we get

$$-d(\text{S}_2\text{O}_8^{2-})/dt = k_d(\text{S}_2\text{O}_8^{2-})$$

Hence  $k_d = k_1[1 - (k_{-1})/(k_{-1} + k_D)]$ ; i.e.,  $k_d < k_1$ .

If  $k_{-1} \gg k_D$ , then  $k_d = 0$ , i.e., no persulfate has decomposed which is not supported by the experimental data. If  $k_D \gg k_{-1}$ , then

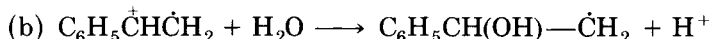
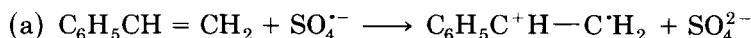
$$k_d = k_1[1 - k_{-1}/k_D] \approx k_1$$

which suggests irreversible dissociation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions. The two SO<sub>4</sub><sup>•-</sup> ion radicals may repel each other inside the solvent cage, and diffuse out of the cage as soon as they are formed. According to Noyes,<sup>23</sup>  $k_1$  and  $k_{-1}$  cannot be measured by the classical reaction kinetics.

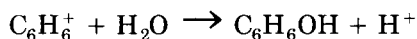
Incidentally, it may be pointed out that the bimolecular decomposition of persulfate, viz.,



has been suggested by Fronaeus and Ostman<sup>31</sup> in order to explain the Ce(III) oxidation to Ce(IV) by persulfate. This work was criticized by Wilmarth and Haim,<sup>32</sup> and has been discussed at length by Behrman and Edwards,<sup>2</sup> who interpreted the results of Crematy<sup>33</sup> obtained from the S<sub>2</sub>O<sub>8</sub><sup>2-</sup>-H<sub>2</sub>O-styrene system by stating that the acid produced in the presence of styrene was possibly due to the reaction of Fronaeus et al. Behrman and Edwards did not consider the fact<sup>34</sup> that in the styrene system H<sup>+</sup> ions are also produced due to the following reactions:



Even in the case of benzene-SO<sub>4</sub><sup>•-</sup> system,<sup>35</sup> H<sup>+</sup> ions are formed by the reaction



The work of Crematy seems to be very complicated and does not have a clear interpretation.

We have shown recently<sup>14</sup> that the pH of an aqueous solution of acrylonitrile and persulfate did not alter at 50°C in the presence of N<sub>2</sub> gas. This shows clearly that the reaction of Fronaeus et al. is not important.

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### References

1. D. A. House, *Chem. Rev.*, **62**, 185 (1962).
2. E. J. Behrman and J. O. Edwards, *Rev. Inorg. Chem.*, **2**, 179 (1980).
3. W. K. Wilmarth, N. Schwartz, and C. R. Giuliano, *Co-ord. Chem. Rev.*, **51**, 243 (1983).
4. F. A. Bovey, I. M. Kolthoff, A. I. Medalia, and E. J. Meehan, *Emulsion Polymerization*, Wiley-Interscience, New York, 1955.
5. D. C. Blackley, *Emulsion Polymerization*, Applied Science, London, 1975.
6. M. G. Evans and J. H. Baxendale, *Trans. Faraday Soc.*, **42**, 197 (1946).
7. C. E. M. Morris and A. G. Parts, *Makromol. Chem.*, **119**, 212 (1968).
8. B. W. Brooks and B. O. Mäkinen, *Makromol. Chem.*, Rapid Commun. **2**, 69 (1984).
9. J. Neelsen, W. Jaeger, G. Reinisch, and H. J. Schneider, *Acta Polym.* **38**, 1 (1987).
10. (a) A. S. Dunn, in *Emulsion Polymerization*, I. Piirma, Ed., Academic, New York, 1982, p. 221; (b) A. S. Dunn and L. C.-H. Chong, *Br. Polym. J.* **2**, 49 (1970).
11. M. Litt, R. Patsiga, and V. Stannett, *J. Polym. Sci. A-1*, **8**, 3607 (1970).
12. Kuanhsiung Chang, Ph.D. thesis, Case Western University, 1980, University Microfilms, also in *Emulsion Polymerization of Vinyl Acetate*, M. S. El-Aasser and J. W. Vanderhoff, Eds., Applied Science, London, 1981.
13. M. S. Adhikari, S. Sarkar, M. Banerjee, and R. S. Konar, *J. Appl. Polym. Sci.*, **34**, 109 (1987).
14. S. Sarkar, M. S. Adhikari, M. Banerjee, and R. S. Konar, *J. Appl. Polym. Sci.*, **35**, 1441 (1988).
15. M. Banerjee, U. S. Satpathy, T. K. Paul, and R. S. Konar, *Polymer (London)*, **22**, 1729 (1981).
16. I. M. Kolthoff and E. M. Carr, *Anal. Chem.*, **25**(2), 298 (1953).
17. S. R. Palit and S. K. Dass, *Proc. Roy. Soc. (London)*, **A226**, 82 (1954).
18. S. K. Dass, S. R. Chatterjee, and S. R. Palit, *Proc. Roy. Soc. (London)*, **A227**, 252 (1955).
19. M. Banerjee and R. S. Konar, *Polymer (London)*, **27**, 147 (1986).
20. S. R. Palit and T. Guha, *J. Polym. Sci.*, **34**, 243 (1959).
21. (a) A. S. Dunn and W. A. Al-Shahib, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 677 (1978); in *Polymer Colloids—II*, R. M. Fitch, Ed., Plenum, New York, 1980, p. 619; (b) S. P. Harrold, *J. Colloid Sci.*, **15**, 280 (1960).
22. P. A. Taylor, Ph.D. thesis, Manchester Univ., U.K., 1965; A. S. Dunn and P. A. Taylor, *Makromol. Chem.*, **83**, 207 (1965).
23. R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955); **78**, 5486 (1956).
24. V. D. McGinniss and A. F. Kah, *J. Coatings Technol.*, **49**, 61 (1977).
25. D. E. Pennington and A. Haim, *J. Am. Chem. Soc.*, **90**, 3700 (1968).
26. A. M. North, in *The International Encyclopedia of Physical Chemistry and Chemical Physics*, E. A. Guggenheim, J. E. Meyer, and F. C. Tompkins, Eds., Pergamon, Oxford, 1966, Vol. 1, Topic 17.
27. S. Sarkar, M. S. Adhikari, M. Banerjee, and R. S. Konar, *J. Appl. Polym. Sci.* **35**, 1441 (1988).
28. M. K. Lindemann, in *Vinyl Polymerization*, G. E. Ham, Ed., Dekker, New York, 1967, Vol. 1, Part I, p. 207.



29. M. Nomura, M. Harada, Eguichi, and S. Nagata, in *Emulsion Polymerization*, ACS Symposium Series No. 24, I. Piirma and J. L. Gardon, Eds, Am. Chem. Soc., Washington, DC, 1976, p. 101.
30. M. Nomura, in *Emulsion Polymerization*, I. Piirma, Ed., Academic, New York, 1982, p. 191.
31. S. Fronaeus and C. O. Ostman, *Acta. Chem. Scand.*, **9**, 902 (1955); **22**, 2827 (1968).
32. W. K. Wilmarth and A. Haim, in *Peroxide Reaction Mechanism*, J. O. Edwards, Ed., Wiley-Interscience, New York, 1962, pp. 180-182.
33. E. P. Crematy, *Experientia*, **26**, 124 (1976).
34. A. Ledwith and P. J. Russel, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 109 (1976).
35. H. Zemel and R. W. Fessenden, *J. Phys. Chem.*, **82**, 2670 (1978); P. Neta, V. Madhavan, H. Zemel, and R. W. Fessenden, *J. Am. Chem. Soc.*, **99**, 163 (1977).

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