

Thermal Decomposition of Potassium Persulfate in Aqueous Solution at 50°C in an Inert Atmosphere of Nitrogen in the Presence of Acrylonitrile Monomer

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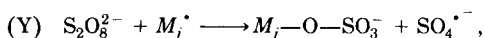
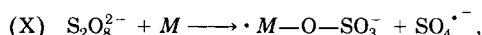
Synopsis

The rate of thermal decomposition of persulfate in aqueous solution in the presence of acrylonitrile (AN) monomer (M) and of nitrogen, may be written as:

$$-d(\text{S}_2\text{O}_8^{2-})/dt \propto (\text{S}_2\text{O}_8^{2-})^{1.35 \pm 0.05} \times (M)^{1.26 \pm 0.069}$$

in the concentration range of persulfate $(1.8 \text{ to } 18.0) \times 10^{-3} \text{ mol dm}^{-3}$, and of monomer (M), 0.30 to 1.20, mol dm^{-3} .

It was observed that the pH of the solution containing persulfate and monomer did not alter during polymerization if the monomer concentrations were close to its solubility under the experimental conditions. Conductance of the aqueous solutions of persulfate and monomer was found to decrease during the reactions. In an unbuffered aqueous solution containing only persulfate, however, the pH was found to decrease continuously at 50°C with time, while the conductance of the solution was found to increase. The monomer (AN) had no effect on the glass electrodes of the pH meter in aqueous solutions, and also on the electrodes of the conductivity cell. It has been suggested that the secondary or induced decompositions of persulfate were due to the following elementary reactions:



where (M_j^{\cdot}) radicals ($j = 1 \text{ to } 10$) are water-soluble oligomeric or polymeric free radicals. k_x and k_y at 50°C have been estimated as 1.70×10^{-5} and $5.08 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. By measuring pH of freshly prepared persulfate solutions at 25°C, it is suggested that 0.05–0.30% of persulfate reacts molecularly with water (i.e., hydrolysis), as soon as it (10^{-3} to $10^{-2} \text{ mol dm}^{-3}$) is added to distilled water (pH 7.0). This hydrolysis was found to be stopped in dilute sulfuric acid solution (pH 3–4).

INTRODUCTION

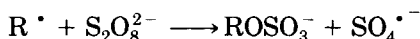
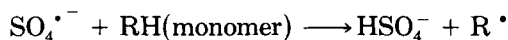
It has been reported recently^{1,2} that vinyl monomers, detergents, and other organic compounds accelerate the thermal decomposition of potassium persulfate in aqueous solutions, but the mechanism of such reactions has not yet

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been established in the persulfate-vinyl monomer system. Morris and Parts¹ and Brooks and Mekanjuola² believe that a vinyl monomer in aqueous solution accelerates the rate constant (k_1) of the Evans-Baxendale reaction³ viz.:



Their experimental work was limited and so they did not suggest any reaction mechanism. Bovey et al.⁴ and Blackley⁵ have suggested that a vinyl monomer would not react directly with the persulfate ion in aqueous or emulsion polymerization, but the $\text{SO}_4^{\bullet-}$ radicals would only initiate polymerization reactions. If the reverse reaction of (1) is not important in the persulfate decomposition,^{4,5} then the initial rate of persulfate decomposition would be independent of monomer concentrations, which has not yet been verified experimentally. Dunn,⁶ on the other hand, believes that vinyl monomers do not alter k_1 and the accelerated rate of persulfate decomposition is due to the following chain reaction, viz.:



in the aqueous phase. Dunn's hypothesis suggests that the pH of the aqueous solution containing monomer and persulfate should decrease with increasing monomer concentrations, and this is open to experimental verification. In order to establish the mechanism of vinyl polymerization initiated by persulfate in aqueous solution or in emulsion, we have investigated the mode of persulfate decomposition analytically in detail in the presence of acrylonitrile (AN) in aqueous solution at 50°C, and some results are reported here.

EXPERIMENTAL

The thermal decomposition of potassium persulfate in aqueous solution in the presence of AN and of N_2 gas, as well as the polymerization of AN have been studied in a 1-L round-bottom Pyrex flask fitted with a Hg-seal stirrer, a dilatometer, and side tubes for passing nitrogen and for extracting solutions under nitrogen pressure for analysis.^{7,8} If the polymer was a precipitate, the reaction was carried out in 250-mL conical flasks fitted with magnetic stirrer and nitrogen passing arrangements. Polymerizations were studied dilatometrically as well as gravimetrically.⁸ To avoid complications during polymerizations, no buffer solutions were used. Undecomposed persulfate as a function of time was estimated by the method of Kolthoff and Carr,⁹ after separating the polymer from the aqueous phase. The volume of the mixture in a conical flask before polymerization was 100 mL, including the monomer, and after polymerization the volume of the filtrate was made exactly 100 mL by washing the polymer with cold distilled water. pH, conductivity, and total quantity persulfate which remained undecomposed in the filtrate were estimated at 25°C.

The reagents were all BDH, E. Merck, and SM (India), AR/GR grade. Potassium persulfate was recrystallized thrice from double-distilled water.

The monomer was distilled just before use to avoid peroxide formation. Expanded scale pH-Meter (of M/s Systronics, Calcutta, Model No. 331) and conductivity meter of the same Company, Model No. 303, were used, and they were calibrated against a series of buffer solutions and of standard KCl solutions, respectively.¹⁰ GR-grade benzene of E. Merck (India) was made thiophene free,¹¹ and distilled before use. Water was distilled twice from alkaline permanganate solutions.¹² The pH of the distilled water used, was found to vary between 6.90 and 7.0 at $(25 \pm 5^\circ\text{C})$, and no attempts were made to remove the dissolved carbon dioxide. The conductance of the distilled water was found to vary between $(0.8 \text{ to } 2.0) \times 10^{-6} \text{ ohm}^{-1}$. It had been observed that an aqueous solution of AN $(0.3\text{--}1.20 \text{ mol dm}^{-3})$ did not alter the pH and conductivity of distilled water.

RESULTS

The effects of various monomers and of benzene on the thermal decomposition of persulfate in aqueous solutions at 50°C are shown in Figure 1. All the organic compounds used were found to accelerate the thermal decomposition of persulfate. The variations of pH (measured at 25°C) of a persulfate solution at 50°C as a function of time and of conductance (also measured at 25°C) of the solution as a function of time are shown in Figure 2. It is found that the pH of the reaction mixture decreased continuously with time, while the conductance of the solution was found to increase with time. The concentra-

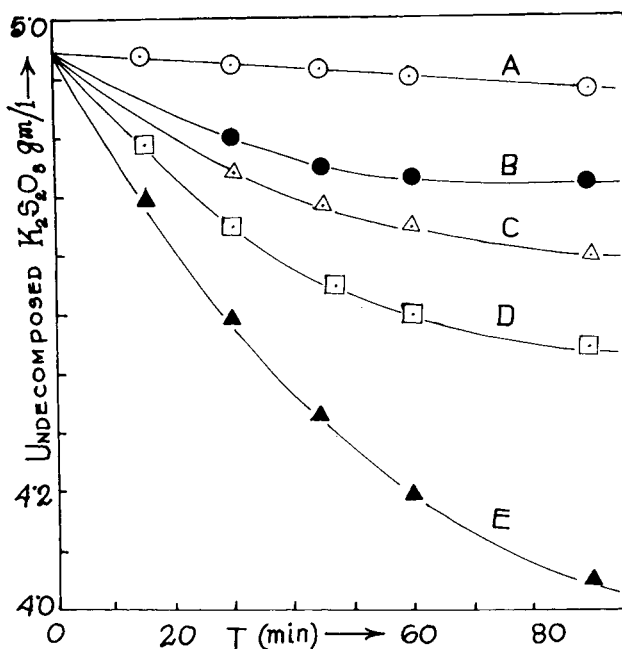


Fig. 1. Thermal decomposition of potassium persulfate ($1.80 \times 10^{-2} \text{ mol dm}^{-3}$) in aqueous solutions at 50°C in nitrogen atmosphere in the absence and the presence of various organic compounds: (A) persulfate only, (B) in the presence of 2% (v/v) benzene, (C) 2% (v/v) styrene, (D) 1.5% (v/v) methyl methacrylate, and (E) 8% (v/v) acrylonitrile.

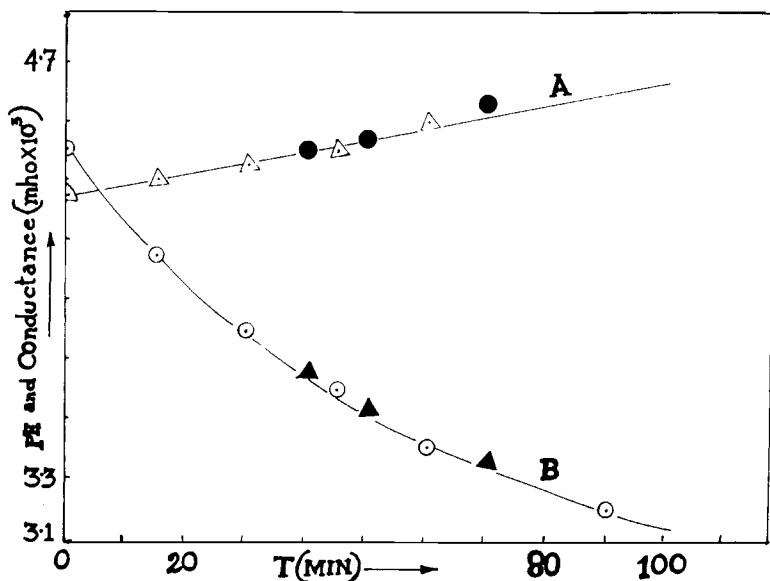


Fig. 2. Variation of pH and conductance of persulfate ($1.82 \times 10^{-2} \text{ mol dm}^{-3}$) solution at 50°C with time in the presence of N_2 . At various intervals of time, the samples were withdrawn from the reaction flask under N_2 pressure, cooled immediately in ice water, and pH and conductance were measured at 25°C . (A) Conductance: (Δ) experimental, and (\bullet) estimated from the amount of persulfate decomposed. (B) pH: (\circ) experimental, and (\blacktriangle) estimated from the amount of persulfate decomposed.

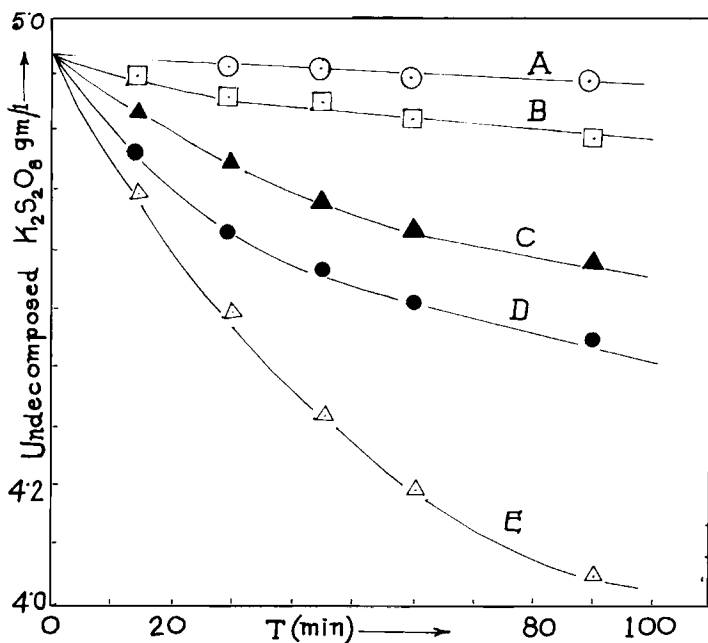


Fig. 3. Concentration effects of acrylonitrile on the thermal decomposition of persulfate ($1.82 \times 10^{-2} \text{ mol dm}^{-3}$): (A) persulfate alone, (B) in the presence of $0.30 \text{ (mol dm}^{-3}\text{) AN}$, (C) $0.60 \text{ (mol dm}^{-3}\text{) AN}$, (D) $0.90 \text{ (mol dm}^{-3}\text{) AN}$, and (E) $1.20 \text{ (mol dm}^{-3}\text{) AN}$.

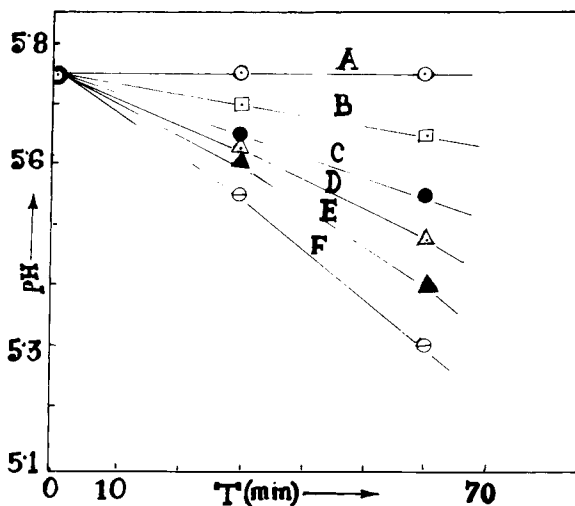


Fig. 4. Effect of AN concentrations on the pH of persulfate solutions (10^{-3} mol dm^{-3}). Reaction was carried out at 50°C , and the pH was measured at 25°C . (A) in the presence of 1.20 (mol dm^{-3}) AN, (B) 0.90 (mol dm^{-3}) AN, (C) 0.60 (mol dm^{-3}) AN, (D) 0.48 (mol dm^{-3}) AN, (E) 0.30 (mol dm^{-3}) AN, and (F) persulfate alone.

tion effects of AN on the thermal decomposition of persulfate are shown in Figure 3, which shows clearly that the rate of persulfate decomposition increased with the increase of AN concentrations. Figures 4 and 5 show the effects of AN concentrations on the pH and on the conductance of the media, respectively, during the thermal decomposition of persulfate. Increase of AN concentrations reduced the rate at which the pH decreased until, when the

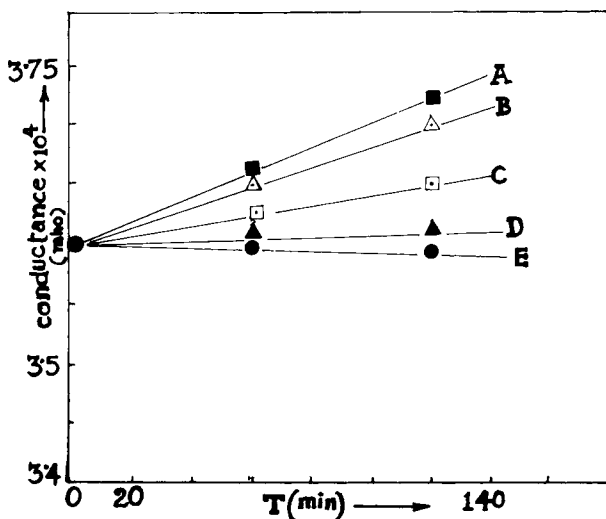


Fig. 5. Effect of AN concentrations on the conductance of persulfate solutions (10^{-3} mol dm^{-3}): (A) persulfate alone, (B) 0.30 (mol dm^{-3}) AN, (C) 0.49 (mol dm^{-3}) AN, (D) 0.60 (mol dm^{-3}) AN, and (E) 1.20 (mol dm^{-3}) AN. The reaction was carried out at 50°C , but the conductance was measured at 25°C .

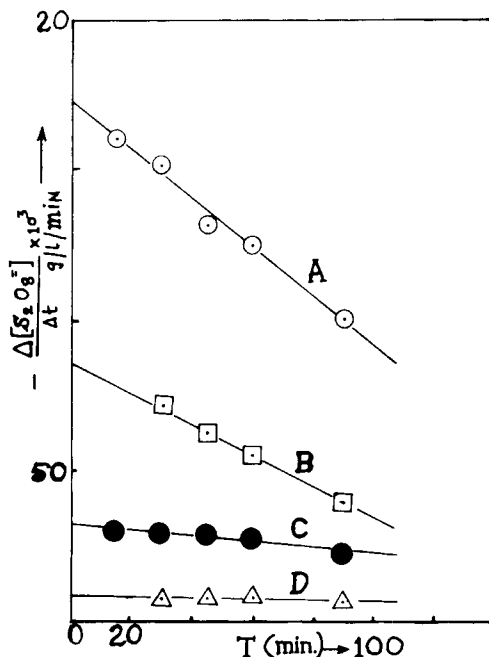


Fig. 6. Determination of initial rate of persulfate decompositions at a given concentration of AN (1.20 mol dm^{-3}), and at (B) $9.2 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$, (C) $4.6 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$, and (D) $1.82 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$.

solution was saturated with AN, no change in pH with time was observed. The conductance of the solution was found to decrease with time in the presence of AN.

Initial rates of persulfate decompositions were determined by drawing tangent to the conversion-time curves at the origin by the Hinshelwood method, and also by plotting the average rate of decompositions as a function of time at the early stages of the reaction (Fig. 6) and extrapolating the resulting straight line by the least-squares method to zero time.¹³ It was assumed that limit t (time) tends to zero, the time average rate at zero time would be a measure of initial rate, namely $-d(\text{S}_2\text{O}_8^{2-})/dt$. The two methods gave approximately the same results within $\pm 10\%$, depending on how accurately we could draw the conversion-time curves, and the tangent to the curves at the origin. The second method however gave reliable and reproducible results. In Figures 7 and 8, conventional order plots for the rate expressions are shown:

$$-d(\text{S}_2\text{O}_8^{2-})/dt \propto (M)^x \times (\text{S}_2\text{O}_8^{2-})^y$$

where x was found to be 1.26 ± 0.069 , and y was 1.35 ± 0.05 .

It has been observed that when persulfate is added to distilled water (pH 7.0), the pH of the water decreases almost instantaneously. Some results are shown in Table I.

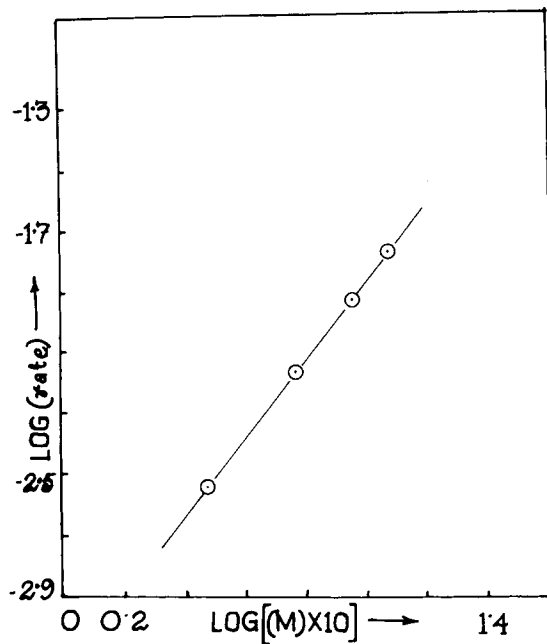


Fig. 7. Order plot for the monomer from

$$-d(S_2O_8^{2-})/dt \propto (M)^x,$$

The slope of the line, log (rate) versus log (M), was 1.26.

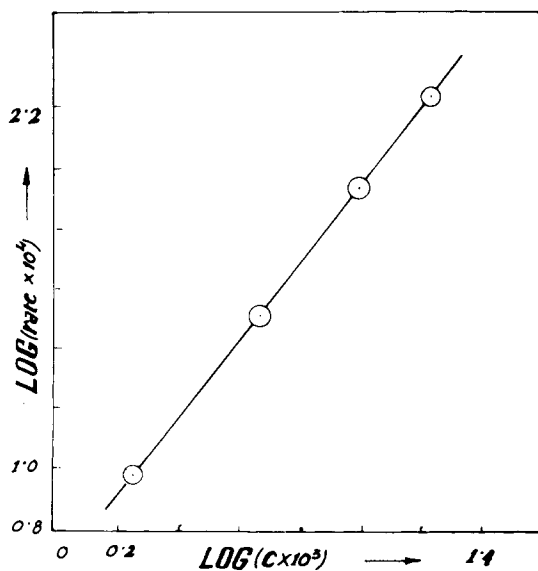


Fig. 8. Order plot for the initiator. Order of persulfate was found to be 1.35.

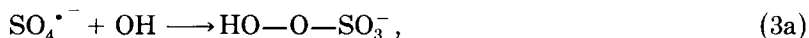
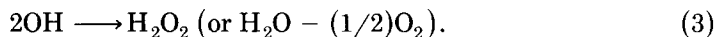
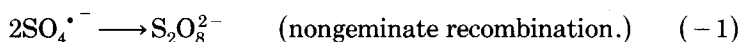
TABLE I
Effects of Persulfate^a and of Sulfate^a on the pH of Double-Distilled Water (pH 7.0 at 25°C)

Serial no.	K ₂ SO ₄ mol dm ³	pH	K ₂ S ₂ O ₈ mol dm ³	pH	Ionic strength in mol dm ⁻³ units
(1)	0.05	5.80	0.05	3.55	0.15
(2)	0.01	6.35	0.01	4.50	0.03
(3)	0.005	6.55	0.005	5.00	0.015
(4)	0.001	6.75	0.001	5.70	0.003

^aRecrystallized thrice from double-distilled water.

DISCUSSION

It is believed that the thermal decompositions of persulfate in aqueous solutions (neutral or slightly alkaline, pH 7–8) take place according to the following free radical mechanism^{3-7,14-17}:



The value of k_1 is very uncertain. At a given temperature, it is a function of pH, and has maximum value at about pH 7 according to Breuer and Jenkins.¹⁸ Bovey et al.⁴ gave $k_1 = 3.5 \times 10^{16} \times \exp(-33,500/1.987 T) \text{ s}^{-1} = 0.75 \times 10^{-6} \text{ s}^{-1}$ at 50°C. We have estimated the Arrhenius parameters of (1) from the data of Kolthoff and Miller¹⁷ by the least-squares treatment of $(\ln k_1)$ versus $(1/T)$, and found $k_1 = 10^{17.1099} \exp(-34,153/1.987 T) \text{ s}^{-1}$ at pH 13 (in 0.1 *N* NaOH solution), and $k_1 = 1.0 \times 10^{-6} \text{ s}^{-1}$ at 50°C. Banerjee and Konar¹⁶ gave $k_1 = 10^{12.903} \exp(-27,600/1.987 T) \text{ s}^{-1} = 1.70 \times 10^{-6} \text{ s}^{-1}$ at 50°C at pH 7 to 8, while Bawn and Margerison¹⁹ found $k_1 = 3.7 \times 10^{13} \times \exp(-28,300/1.987 T) \text{ s}^{-1} = 2.619 \times 10^{-6} \text{ s}^{-1}$ at 50°C (pH = 7–8). Morris and Parts¹ and Blackley⁵ gave $k_1 = 1.40 \times 10^{-6} \text{ s}^{-1}$ at the same temperature. Ball et al.²⁰ estimated $k_1 = 1.33 \times 10^{-6} \text{ s}^{-1}$, and Kao et al.²¹ used k_1 as $1.57 \times 10^{-6} \text{ s}^{-1}$ at 50°C. Breuer and Jenkins¹⁸ reported that the reaction (1) had activation energy as 24 kcal/mol at pH 7 and 35.0 kcal/mol at pH 13. In the pH range 4–7, we have found that k_1 remained almost constant within experimental error at 50°C, and k_1 was found as $2.61 \times 10^{-6} \text{ s}^{-1}$. Furthermore, addition of K₂SO₄ ($4 \times 10^{-3} \text{ mol dm}^{-3}$) had no measureable effect on the rates of persulfate decomposition ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) in the same pH range (4–7).

The entropy of activation estimated from the data of Banerjee and Konar¹⁶ is about $-6.88 \text{ J/mol/}^\circ\text{K}$, and that from the data of Bawn and Margerison¹⁹

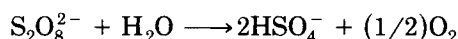
TABLE II
Decomposition of Potassium Persulfate in Aqueous Solution at 50°C

Time (min)	$(S_2O_8^{2-})$ decomposed (mol dm ⁻³) × 10 ⁴ (A)	$\Delta(H^+)_t$ from A × 10 ⁴ , (g ions dm ⁻³)	$(H^+)_t = [(H^+)_0 + \Delta(H^+)_t] \times 10^4$ (B)	pH estimated from (B)	pH measured
0	0	0	0.398	4.40	4.40
45	1.11	2.22	2.620	3.58	3.60
60	1.85	3.70	4.10	3.38	3.40
90	2.59	5.18	5.58	3.23	3.20
120	3.33	6.66	7.16	3.15	3.10

Initial concentration (C_0) of persulfate 1.8333×10^{-2} mol dm⁻³, pH at zero time was 4.40, and this gave $(H^+)_0 = 0.398 \times 10^{-4}$ g ions dm⁻³.

is 5.85 J/mol/°K, at 50°C and at pH 7–8. Since the entropy of activation is not far from zero, it implies that the structure of the persulfate ion in the activated state is not very different from its ground state structure. We assume that a persulfate ion is vibrationally excited in the activated state, and the peroxide bond being stretched to the critical length during vibrations, breaks up homolytically. It is clear from the work of Breuer and Jenkins,¹⁸ that Kolthoff's data at pH 13 would not be applicable to the reaction at lower pH. At pH 7, Breuer and Jenkins gave $k_1 = 10^{12.689} \times \exp(-24000/1.987 T)$ $s^{-1} = 2.81 \times 10^{-6} s^{-1}$ at 50°C.

This mechanism predicts that the pH of the medium would decrease with time during the thermal decompositions of persulfate in an unbuffered aqueous solution. Reaction (2) is a pseudo unimolecular first-order one, and k_2 at 25°C has been reported^{22,23} as $10^3 \leq k_2 \leq 10^4 s^{-1}$. We assume that k_2 at 50°C would be $10^4 s^{-1}$. The conductance of the solution would also increase since H^+ ions produced in the reaction, $HSO_4^- \rightarrow H^+ + SO_4^{2-}$, have higher conductance, and a persulfate ion is replaced by $2H^+$ ions and $2SO_4^{2-}$ ions. These expectations are confirmed by the data of Figure 2. Table II gives a comparative study between the H^+ ions measured from persulfate decompositions estimated iodometrically and those estimated by direct pH measurements. The agreement seems to be satisfactory, but it is found that the value of k_1 would be $2.61 \times 10^{-6} s^{-1}$ at 50°C as reported by Bawn and Margerison.¹⁹ Note: $(H^+)_t$ was calculated from the overall reaction



and all the HSO_4^- ions would dissociate into H^+ ions and SO_4^{2-} , if its concentration is less than $10^{-3} mol dm^{-3}$ according to Cotton and Wilkinson.²⁴

In the thermal decomposition studies of persulfate in aqueous media, it was assumed^{4-7,14-20} that the reaction (-1) would not be important even inside the solvent cage or outside the cage. According to Noyes,²⁵ primary recombination of uncharged free radicals inside a nonpolar solvent cage takes place within $10^{-13} s$ after their formation, and secondary recombination inside the cage within 10^{-9} to $10^{-11} s$. Only highly reactive scavengers can compete with the secondary recombination process. Water appears to be a poor scavenger for $SO_4^{\bullet-}$ radicals, since less than 0.50% persulfate is decomposed in water (pH 7) in 1 h at 50°C. Assuming that the Noyes' Cage Effect is also applicable to charged free radicals in highly polar solvents, the primary and secondary recombination of geminate $SO_4^{\bullet-}$ radicals are so fast, that only a very small amount of persulfate is decomposed in a given time. A very small fraction of $SO_4^{\bullet-}$ radicals would diffuse out of the solvent cage into the bulk phase where they would react with solvent, scavengers, and other radicals. Further Noyes has pointed out that the classical reaction kinetics would not be able to describe the primary and the secondary recombination of cage radicals. Probably because of these factors, it is assumed that the cage recombination of $SO_4^{\bullet-}$ radicals is not important.⁵⁰

k_{-1} has been estimated as $(3.7 \text{ to } 8.8) \times 10^8 dm^3 mol^{-1} s^{-1}$ at 25°C from photochemical experiments.^{22,26,27} If the activation energy for free radical recombination be taken as zero, k_{-1} will be independent of temperature.

Considering reactions (1) to (3a)

$$\begin{aligned} d(\text{SO}_4^{\bullet-})/dt &= 2k_1(\text{S}_2\text{O}_8^{2-}) - 2k_{-1}(\text{SO}_4^{\bullet-})^2 - k_2(\text{SO}_4^{\bullet-}) - k_{3a}(\text{SO}_4^{\bullet-})(\text{OH}) \\ &= 0 \text{ in the steady state (S.S)} \end{aligned}$$

and,

$$d(\text{OH})/dt = k_2(\text{SO}_4^{\bullet-}) - 2k_3(\text{OH})^2 - k_{3a}(\text{SO}_4^{\bullet-})(\text{OH}) = 0 \text{ (in SS)}$$

Solving for $(\text{SO}_4^{\bullet-})$ radicals, we get

$$(\text{SO}_4^{\bullet-}) = (-k_2/2k_{-1}) \pm \frac{[k_2^2 + 4k_{-1}\{k_3(\text{OH})^2 + k_1(\text{S}_2\text{O}_8^{2-})\}]^{1/2}}{2k_{-1}}$$

If all the $\text{SO}_4^{\bullet-}$ radicals of (1) disappear via (2), and all OH radicals produced in (2) disappear via (3), then to a good approximation, $k_3(\text{OH})^2 = k_1(\text{S}_2\text{O}_8^{2-})$, and hence

$$(\text{SO}_4^{\bullet-}) = (-k_2/2k_{-1}) \pm \frac{[k_2^2 + 8k_1k_{-1}(\text{S}_2\text{O}_8^{2-})]^{1/2}}{2k_{-1}}$$

Taking,

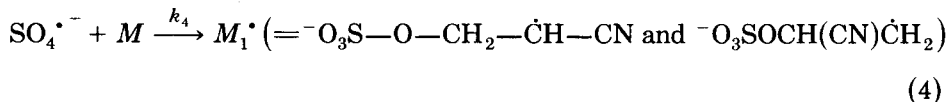
$$k_2 = 10^4 \text{ s}^{-1}, \quad k_1 = 2.61 \times 10^{-6} \text{ s}^{-1}$$

and $k_{-1} = 8.8 \times 10^8 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, it is found that

$$k_2^2 \gg \{8k_1k_{-1}(\text{S}_2\text{O}_8^{2-})\}, \text{ if } (\text{S}_2\text{O}_8^{2-}) = 10^{-2} (\text{mol dm}^{-3}).$$

This means that either $(\text{SO}_4^{\bullet-}) = \text{zero}$, or negative, that is $(-k_2/k_{-1})$. Hence it appears to us that (-1) will not be important as found by others.¹⁵

In the presence of monomer (M), $\text{SO}_4^{\bullet-}$ radicals will undergo parallel reactions, viz. (2) and (4),

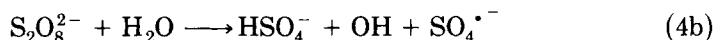
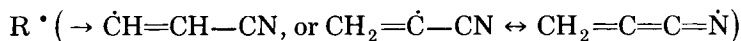


k_4 has been estimated^{28,29} at 25°C as $8.1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Assuming an activation energy of about 5 kcal/mol for free radical addition to olefins,³⁰ $k_4 = 3.764 \times 10^{11} \times \exp(-5000/1.987 T) = 1.56 \times 10^8$ at 50°C in $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. If the monomer concentration be 1.60 mol dm^{-3} , then the rate of (2)/rate of (4) = 4.0×10^{-5} . This shows clearly that the reaction (2) will be totally suppressed, if the aqueous solution is saturated with the acrylonitrile monomer. Since the pH of the solution does not change (Fig. 4) at relatively

higher concentration of AN, it appears that neither the reaction (4a) nor (4b) occurs to any significant extent.



where



as suggested by Fronaeus and Ostman³¹ and Crematy.³² If persulfate decomposes only via (1) in the presence of monomer, then after 1 h, the concentration of undecomposed persulfate should be, $C_t = C_0 \exp(-k_1 t) = 1.833 \times 10^{-2} \times \exp(-2.61 \times 10^{-6} \times 3600) = 1.816 \times 10^{-2} \text{ mol dm}^{-3}$, while the experimentally measured value of C_t was $1.556 \times 10^{-2} \text{ mol dm}^{-3}$. Further, the rate of persulfate decomposition was found to increase with the increase of AN concentrations (Fig. 3). All these facts indicate that persulfate decompositions took place through other paths in addition to (1), in the presence of AN. Since the pH of the solution was above 3, the acid-catalyzed decomposition of persulfate would not be important according to Kolthoff et al.^{4,17} It may be mentioned here that Bacon also noted that an aqueous solution of AN (5.0% by weight) did not affect glass electrodes of PH-meters, and the pH of the solution did not change during polymerizations initiated by persulfate.³³

By measuring the pH change of the solution at various concentrations of AN and at the early stages of the reaction, we have estimated the fraction of $\text{SO}_4^{\bullet -}$ radicals reacting with water at 50°C in the presence of various amounts of AN, and the results are shown in Table III.

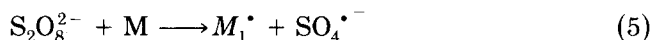
During the reactions in the presence of and absence of AN, $\text{SO}_4^{\bullet -}$ radicals would produce H^+ ions and SO_4^{2-} ions via reaction (2); if the free radicals are removed by the monomer molecules via (4), the pH of the solution would

TABLE III
Change in H^+ Ion Concentrations After 30 min. of the Reaction in Nitrogen Atmosphere.
Recipe: $\text{K}_2\text{S}_2\text{O}_8 = 10^{-3} \text{ mol dm}^{-3}$, AN Concentration Varies,
and Total Volume was 100 cm^3 (Temp. 50°C)

(AN) in mol dm^{-3}	Change in H^+ ion concentrations (in gm ions dm^{-3}) ^a $\times 10^5$	Percent of $\text{SO}_4^{\bullet -}$ radicals reacted with water
0.00	0.104	100.00
0.30	0.0734	70.58
0.455	0.0593	57.02
0.603	0.0461	44.33
0.905	0.0217	20.87
1.200	0.00	0.00

^a $-\Delta\text{pH} = \text{pH of the persulfate solution after 30 min. of the reaction at } 50^\circ\text{C, (and measured at } 25^\circ\text{C)} - \text{pH of the freshly prepared persulfate solution at } 25^\circ\text{C. From this } \Delta\text{pH, change in hydrogen ion concentration was estimated, and it was assumed that all the } \text{H}^+ \text{ ions came from the reaction (2).}$

increase while the conductance of the solution would decrease and this hypothesis is qualitatively consistent with our experimental results shown in Figure 5. Since the rate of persulfate decomposition was accelerated at the outset in the presence of AN and other organic compounds (Figs. 1 and 3), it seems that the reaction (5) may also be important,



Very recently, such a hypothesis had been revived by Bataile et al.³⁴ in the emulsion polymerization of styrene, although it was originally rejected by Bovey et al.⁴ and Blackley.⁸ It would be relevant to point out here that Kolthoff and others^{4,35} found that allyl acetate (0.024–0.17 mol dm⁻³) had no effect on the initial rate of persulfate decomposition ($\text{K}_2\text{S}_2\text{O}_8 = 0.01$ mol dm⁻³, pH 6.9, and temp. 70°C, Fig. 1 of Ref. 35), and after 1.5 h, the rate of decomposition of persulfate was found to be accelerated, possibly due to the reaction of poly-allyl acetate and persulfate.³⁵ On the basis of this finding, Kolthoff et al. assumed that the reaction (5) would not be important, even when *M* is a vinyl monomer, alcohol, or any other organic compound. This wrong assumption forced them to conclude that they had no explanation^{4,35} for the order (0.5) of alcohol in the oxidation of (methyl or ethyl) alcohols by persulfate,^{35,36} and for the order of styrene (2nd order) in the persulfate initiated aqueous polymerization of styrene.⁴

In the present case, the rate of persulfate decomposition was accelerated at the outset, and was found to decrease continuously in a given run as the monomer was converted to polymer. This fact suggests that the poly-acrylonitrile latex particles possibly do not react with the persulfate ions. Table IV shows that the rate of persulfate decomposition in a given run decreased with time or conversion of monomer to polymer, which is contrary to the facts observed by Kolthoff et al.³⁵ in the allylacetate-persulfate system.

The following elementary reactions seem to be responsible for the thermal decomposition of persulfate in aqueous solutions and the aqueous polymerization of AN initiated by persulfate. When the water-soluble polymer molecules or radicals would exceed the critical chain length (degree of polymerization may be greater than 10),³⁷ they would separate from the aqueous phase and

TABLE IV
Time Average Rate of Persulfate Decomposition at 50°C in the Presence of AN (1.20 mol dm⁻³)
and $\text{K}_2\text{S}_2\text{O}_8$ (1.8×10^{-2} mol dm⁻³) in Nitrogen Atmosphere

Time interval (min)	$(\text{K}_2\text{S}_2\text{O}_8)_t$ Initial (g/dm ³)	$(\text{K}_2\text{S}_2\text{O}_8)_t$ where <i>t</i> is in min (g/dm ³)	$-\frac{\Delta(\text{S}_2\text{O}_8^{2-})}{\Delta t}$ g/dm ⁻³ s ⁻¹ $\times 10^4$	Percent con- version of monomer to polymer
0–15	(4.95) ₀	(4.71) ₁₅	2.67	(31.65) _{<i>t</i>=15}
15–30	(4.71) ₁₅	(4.495) ₃₀	2.39	(58.68) _{<i>t</i>=30}
30–45	(4.495) ₃₀	(4.36) ₄₅	1.50	(74.60) _{<i>t</i>=45}
45–60	(4.36) ₄₅	(4.20) ₆₀	1.78	(78.75) _{<i>t</i>=60}
60–90	(4.20) ₆₀	(4.05) ₉₀	0.833	(85.00) _{<i>t</i>=90}

aggregate together into latex particles^{37,38} by collision or diffusion mechanism. Homogeneous polymerization on the surface of these latex particles would take place by free radical mechanism as pictured by Smith and Ewart^{4,5} or Medvedev.³⁹ The separating polymer is a stable colloid, and the system follows the kinetics of Emulsion Polymerizations.⁴⁰

REACTION MECHANISM

Reaction	Phase
(1) $S_2O_8^{2-} \longrightarrow 2SO_4^{\bullet -}$	In the aqueous phase and also at the particle- water interface.
(2) $SO_4^{\bullet -} + H_2O \longrightarrow HSO_4^- + OH$,	In the aqueous phase
(3) $2OH \longrightarrow H_2O + (1/2) O_2$,	In the aqueous phase
(4) $SO_4^{\bullet -} + M \longrightarrow M_1^{\bullet}$	In the aqueous phase
(5) $S_2O_8^{2-} + M \longrightarrow M_1^{\bullet} + SO_4^{\bullet -}$,	In the aqueous phase
(6) $M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}$,	In water and also in the latex phase.
(7) $M_j^{\bullet} + M \xrightarrow{k_p} M_{j+1}^{\bullet}$,	In water and also in the latex phase.
(8) $M_j^{\bullet} + M(RH) \xrightarrow{k_{tr} \cdot m} M_jH + R \cdot$,	In water and also in the latex phase.
(9) $(M_j^{\bullet})_w \rightleftharpoons (M_j^{\bullet})_p$,	Particle-water interface.
(10) $(M_j^{\bullet})_w + S_2O_8^{2-} \longrightarrow M_j-O-SO_3^- + SO_4^{\bullet -}$,	In the aqueous phase.
(11) $(M)_w \rightleftharpoons (M)_p$,	At the particle- water interface.
(12) $2(M_j^{\bullet})_w \xrightarrow{k_{tw}} \text{Polymer}$,	In the aqueous phase $j = 1$ to 10 (Ref. 37)
(13) $2(M_i^{\bullet})_p \xrightarrow{k_{ip}} \text{Polymer}$,	In the polymer phase, $i = 1$ to any value.

$(M_j^{\bullet})_w$ are water-soluble oligomeric free radicals. $(M_i^{\bullet})_p$ are radicals present in the latex particles, which may be water soluble or water insoluble (if $i > 10$). If $i = j$, then M_i^{\bullet} and M_j^{\bullet} radicals are the same. It is assumed that radicals having $i > 10$, would be found only in the polymer phase,⁴¹ and k_p is independent of polymer chain length.⁴² From the proposed reaction model, it is evident that

$$-d(S_2O_8^{2-})/dt = k_1(S_2O_8^{2-}) + k_5(S_2O_8^{2-})(M) + k_{10}(M_j^{\bullet})_w(S_2O_8^{2-}), \quad \dots (1)$$

Rate of initiation in the aqueous phase (R_i)_w,

$$(R_i)_w = \{2k_1(\text{S}_2\text{O}_8^{2-}) + 2k_5(M)(\text{S}_2\text{O}_8^{2-}) + k_{10}(M_j^\bullet)_w(\text{S}_2\text{O}_8^{2-})\}V_w, \quad \dots(2)$$

Assuming that (1) and (5) are the major chain initiation reactions, and neglecting (10),

$$(R_i)_w = \{2k_1 + 2k_5(M)\}(\text{S}_2\text{O}_8^{2-})V_w, \quad \dots(3)$$

where V_w = volume fraction of the aqueous phase, and V_p = volume fraction of the polymer phase, that is, $V_w + V_p = 1.0$. Under our experimental conditions, $V_w \gg V_p$, or $V_w \approx 1.0$. Rate of termination in the aqueous phase (R_t)_w, is given by

$$(R_t)_w = 2k_{tw}(M_j^\bullet)_w^2V_w, \quad \dots(4)$$

Equating (3) and (4) in the steady state, we get

$$(M_j^\bullet)_w = k_{tw}^{-1/2}\{k_1 + k_5(M)\}^{1/2} \times (\text{S}_2\text{O}_8^{2-})^{1/2}, \quad \dots(5)$$

Combining (1) and (5), we get

$$\frac{1}{(\text{S}_2\text{O}_8^{2-})} \left\{ -\frac{d(\text{S}_2\text{O}_8^{2-})}{dt} \right\} = \{k_1 + k_5(M)\} + \frac{k_{10}}{k_{tw}^{1/2}} [k_1 + k_5(M)]^{1/2} (\text{S}_2\text{O}_8^{2-})^{1/2} \quad \dots(6)$$

Equation (6) predicts that the orders of AN and of persulfate would be greater than unity, which is consistent with the results presented here. Furthermore, the left-hand side of (6) has been plotted against $(\text{S}_2\text{O}_8^{2-})^{1/2}$, at a given concentration of monomer in Figure 9, and from the slope and intercept of the resulting straight line by the least-squares method, we get $k_{10}^2/k_{tw} = 3.587 \times 10^{-3}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$). Taking k_{tw} as 7.32×10^9 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) from Dainton et al.³⁷, we get k_{10} as 5.08×10^3 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) at 50°C. From the intercept of Figure 9, we get k_5 as 1.70×10^{-5} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$), taking AN concentration 1.20 (mol dm^{-3}), and k_1 as $2.61 \times 10^{-6} \text{ s}^{-1}$ from Bawn and Margerison.¹⁹

Data of Table I show clearly that $\text{S}_2\text{O}_8^{2-}$ ions undergo instantaneous hydrolysis when dissolved in distilled water. It has been observed also that 10^{-2} to 10^{-3} (mol dm^{-3}) $\text{K}_2\text{S}_2\text{O}_8$ in dilute H_2SO_4 acid solution (pH 3.5–3.6), did not change the pH of the acid solution within 24 h at $(27 \pm 3)^\circ\text{C}$. It appears that the hydrolysis of persulfate ions is prevented in acid solutions at room temperature.

Table II shows the agreement between the pH estimated from the amount of persulfate decomposed in a given time, with the experimentally measured pH. The agreement is quite good. Dunn and Chong⁴³ had discussed at length

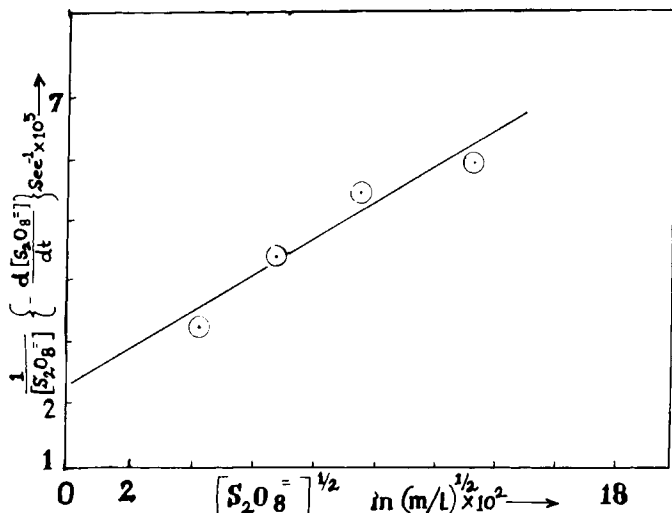


Fig. 9. Plot of left-hand side of Eq. (6) versus $(S_2O_8^{2-})^{0.5}$.

the stability of aqueous solution of persulfate. Data of Table III show that all the primary radicals ($SO_4^{\cdot -}$) will be captured by the monomer molecules, when the aqueous solution will be saturated with monomer. Since the rate of persulfate decomposition decreased with time (Table IV), it confirms the belief that latex particles of polyacrylonitrile are not involved in the induced decomposition of persulfate. Reaction (10) had been suggested by others in the persulfate-initiated emulsion polymerization of vinyl acetate,^{40,44,45} alcohol oxidation.⁴⁹⁻⁵¹

Results of Figure 1 confirm the previous observations that water-soluble organic compounds,^{5,46,47} in general and even sparingly soluble compounds, *viz.* benzene,⁴⁸ styrene, etc. accelerate the decomposition of persulfate ions.

CONCLUSION

The results presented here show clearly that (i) the reaction (5) is also an important initiation reaction for polymerization, (ii) a fraction of water-soluble oligomeric radicals are oxidized by the persulfate ions in the aqueous phase, (iii) the hypothesis that the primary free radicals ($SO_4^{\cdot -}$) would abstract a H atom from a monomer molecule of AN, has no experimental evidence, (iv) the rate of generation of primary radicals in a given run would not remain constant during the polymerization reactions, and (v) AN does not influence the rate constant of persulfate dissociation into two sulfate ion radicals in aqueous solutions.

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