Kinetics and Mechanism of the Thermal Decomposition of Potassium Persulphate Ions in Aqueous Solutions at 50°C in the Presence of Nitrogen Gas and Methacrylonitrile Monomer

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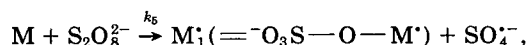
Chemistry Department, Regional Engineering College, Durgapur 713209 West Bengal, India
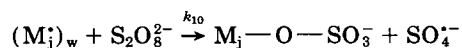
SYNOPSIS

The initial rate of persulphate (I) decomposition at 50°C in the presence of nitrogen and methacrylonitrile (MAN) in an unbuffered aqueous solution (pH 4–7) may be written as:

$$-d(S_2O_8^{2-})/dt \propto (MAN)^{1.29\pm0.05} \times (I)^{1.20\pm0.04}$$

in the concentration ranges of persulphate (I) $(0.25-2.50) \times 10^{-2}$ (m/dm^3) and of (MAN) 0.18–0.36 (m/dm^3). During the reaction, a white substance (polymethacrylonitrile) separates out in the colloidal state or in the precipitate form from the medium depending on the ionic strength of the medium. The pH of the medium was found to decrease rapidly and continuously with time in the absence of methacrylonitrile, but it decreased slowly and continuously with time in the presence of the monomer, MAN. If an additional quantity of MAN is injected late in a run, the rate of persulphate decomposition is further accelerated in a given run. However, the rate of persulphate decomposition is found to decrease continuously in the presence of MAN with time, i.e., as the monomer is converted to polymer. It is suggested that MAN accelerates the decomposition of persulphate ions, due to the following reactions in the aqueous phase:
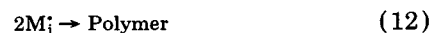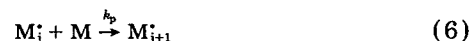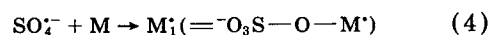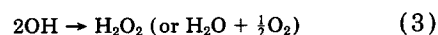
$$M + S_2O_8^{2-} \xrightarrow{k_5} M_1^{\cdot}(= {}^-O_3S - O - M^{\cdot}) + SO_4^{\cdot-},$$

and

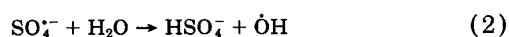$$(M_j^{\cdot})_w + S_2O_8^{2-} \xrightarrow{k_{10}} M_j - O - SO_3^- + SO_4^{\cdot-}$$

where $(M_j^{\cdot})_w$ is a-water soluble oligomeric or polymeric (j = 1–10) free radical. The estimated values of k_5 and k_{10} are 1.05×10^{-5} and 1.14×10^3 (in dm^3/m/s), respectively.

INTRODUCTION

It has been suggested that the thermal decomposition of persulphate ions in aqueous solutions (pH 4–7) in the presence of a vinyl monomer (water soluble or sparingly soluble) would take place according to the following mechanism[1-5]:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot-} \tag{1}$$

$$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^- + \dot{O}H \tag{2}$$

$$2OH \rightarrow H_2O_2 \text{ (or } H_2O + \tfrac{1}{2}O_2) \tag{3}$$

$$SO_4^{\cdot-} + M \rightarrow M_1^{\cdot}(= {}^-O_3S - O - M^{\cdot}) \tag{4}$$

$$M_j^{\cdot} + M \xrightarrow{k_p} M_{j+1}^{\cdot} \tag{6}$$

$$2M_j^{\cdot} \rightarrow \text{Polymer} \tag{12}$$

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It has been assumed[1-5] that reaction (1) is irreversible, and in the presence of the monomer (M) reactions (2) and (3) would not be important. Such a mechanism predicts that

$$-d(S_2O_8^{2-})/dt \propto (M)^0 \times (S_2O_8^{2-})^{1.0}.$$

Very recent reports from this laboratory[6,7] show that the above mechanism of persulphate ion decomposition in the presence of a vinyl monomer and nitrogen gas is highly oversimplified, and actually the initial rate of persulfate ion decomposition at a given temperature and pH of the aqueous solution (4–7), is a function of (1) the nature of the monomer and its water solubility, (2) concentrations in the aqueous phase, and (3) nature of the polymer formed. Dunn[8] suggested that R⁺ radicals (produced from the monomer molecules by SO_4^{-} primary free radicals through H-abstraction) may cause induced chain decomposition of persulphate ions, viz.:

$$SO_4^{-} + M(=RH) \rightarrow HSO_4^{-} + R^{\cdot}$$

$$R^{\cdot} + S_2O_8^{2-} \rightarrow R-O-SO_3^{-} + SO_4^{-}.$$
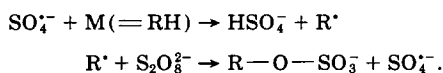
Such a mechanism of the induced decomposition of persulphate indicates that the pH of the solution would decrease with the increase of monomer (RH) concentrations in the aqueous phase. Experimental evidences in the persulphate–acrylonitrile system do not support[7] Dunn's hypothesis. Chang[9] suggested that in the persulphate–vinyl acetate–lauryl sulphate system (i.e., in the persulphate-initiated emulsion polymerization of vinyl acetate) R⁺ monomeric free radicals would be produced in the latex particles due to chain transfer to monomer, and a fraction of water-soluble monomeric free radical of the type R⁺ but not $M_1^{\cdot}$ would get oxidised by the $S_2O_8^{2-}$ ions in the aqueous phase as suggested by Dunn.[8] In those cases, where chain transfer to monomer would not be significant, Chang's mechanism implies that there would be no induced decomposition of persulphate. Experimental evidences[6,7] do not support also the hypothesis of Chang. We report here the results obtained in the thermal decomposition of persulphate ions in unbuffered aqueous solutions (pH 4–7) at 50°C in the presence of methacrylonitrile (MAN) and nitrogen gas. It may be pointed out here that Kolthoff et al.[1,10] found that k_1 at a given temperature did not vary significantly with the change of pH in the range 3–10.

EXPERIMENTAL

The experiments were carried out in a 1-L Pyrex flask fitted with Hg-seal stirrer and nitrogen-passing arrangements, and also in 250-mL conical flasks fitted with nitrogen-passing arrangements and magnetic stirrers at 50 ± 0.10°C in a water thermostat.[6,7] No buffer solutions were used, as traces of metal ions present in the buffer reagents were found to catalyse the decomposition of persulphate. Further, buffer ingredients also interfere with the polymerization process during the reactions. Experimental details have been published elsewhere.[7]

The reagents were of BDH, E. Merck (India), AR/GR grade. Potassium persulphate (E. Merck, GR-grade) was recrystallised twice from double-distilled water. The monomer was received from Fluka (A.G), and was washed with dilute NaOH (1%) solution, then thoroughly with distilled water to make it free from alkali. It was then dried over anhydrous calcium chloride, vacuum distilled, and fractionated. The middle fraction (refractive index 1.401 at 25°C) was collected and stored at −5.0°C. Before use, the monomer was tested for peroxide. If peroxides were detected, it was refluxed in nitrogen atmosphere and distilled before use. pH of the solutions was measured in a pH-Meter (of M/s Systronics, Calcutta, Model-331). It has been noted that an aqueous solution of MAN did not alter the pH of distilled water. During the reaction at 50°C, the samples were collected at different times and cooled immediately in ice. The pH of the solutions was then measured at room temperature (25 ± 3)°C. Persulphate was estimated by the iodometric method of Kolthoff and Carr.[11] Polymerization was studied gravimetrically; molecular weights of polymers were determined viscometrically in dimethyl formamide solvent at 30°C, and using the equation,[12]

$$(\eta) = 0.306 \times (M_n)^{0.503},$$

where (η) is in mL/g and

$$\eta_{sp}/C = (\eta) + K_H(\eta)^2C,$$

the Huggin's constant (K_H) was found to be 0.366; C is the concentration of polymer in N-N-dimethyl formamide solvent in g/100 mL.

RESULTS

The results of persulphate decomposition in the presence of MAN are shown in Figures 1 and 2 and Table I. Figure 1 shows the undecomposed persulphate left in the reactor as a function of time and at various concentrations of the monomer. It is found that the rates of persulphate decomposition were increased with the increase of monomer con-
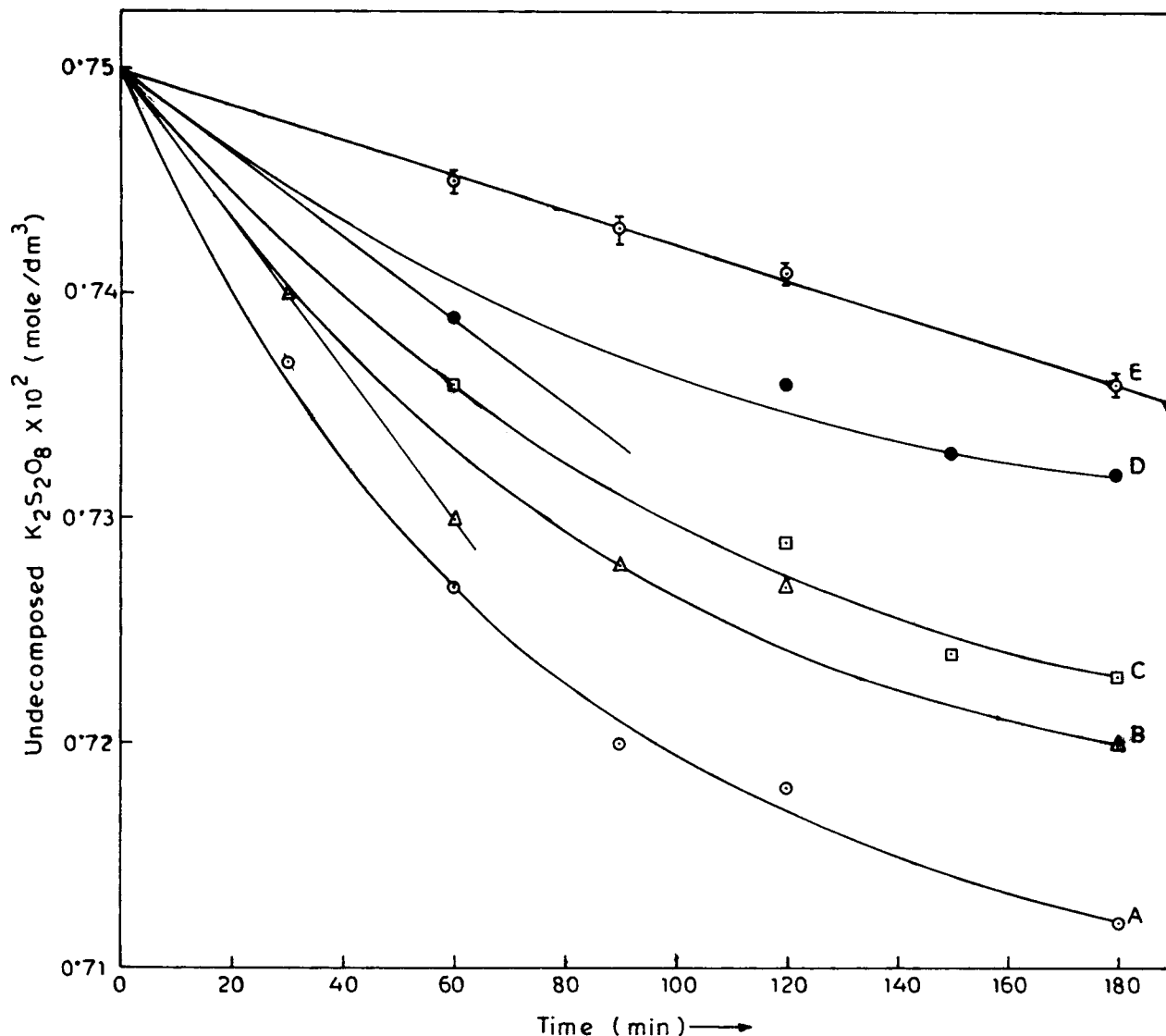
Figure 1 Concentration effects of methacrylonitrile (MAN) on the thermal decomposition of potassium persulphate (0.75×10^{-2} m/dm^3) in aqueous solutions at 50°C in nitrogen atmosphere. A, 0.36; B, 0.30; C, 0.24; D, 0.18 m/dm^3 MAN; E, with persulphate alone.

centrations. Initial rates of persulphate decomposition were estimated at various concentrations of the monomer and at a given concentration of persulphate, by plotting the time average rates of persulphate decomposition as a function of time, and extrapolating the resulting linear plot to zero time (Fig. 3). It is assumed that the intercept would give the initial rate at zero time. It is also found that in the absence of monomer the rate of persulphate decomposition is independent of time (Fig. 1, curve E) at the early stages of the reaction, whereas in the presence of monomer the rates of decomposition were found to decrease with time and with the conversion of monomer to polymer. Initial rates of per-

sulphate decomposition were also determined by the tangent method of Hinshelwood (shown in Fig. 1), and the two rates obtained by the two different methods agree within ±10.0%. Figure 4 shows the conventional order plot of the monomer with respect to the rate of persulphate decomposition, and the order of monomer was found to be 1.29 ± 0.05. Figure 2 shows the time average rates of persulphate decomposition at various concentrations of the persulphate and at a given concentration of the monomer. Figure 5(a) shows the order plot of persulphate with respect to its decomposition, taking initial rates of persulphate decompositions. The order of persulphate was found to be about 1.23. Figure 5(b)
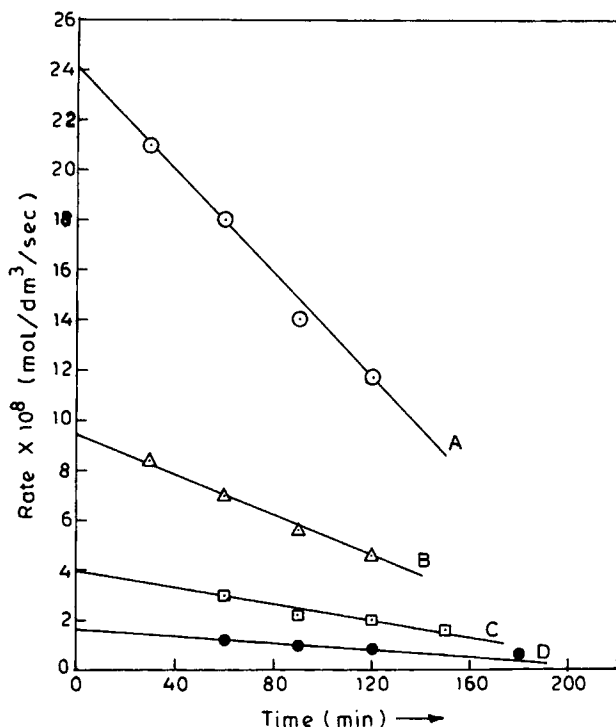
Figure 2 Average rates of persulphate decompositions at various concentrations of persulphates and at a given concentration of the monomer (MAN), 0.36 m/dm³. A, 2.50×10^{-2}; B, 1.0×10^{-2}; C, 0.50×10^{-2}; D, 0.25×10^{-2} (m/dm³) potassium persulphate. It is assumed that the extrapolated rates at zero time are the initial rates at various concentrations of persulphates.

shows the order plot of persulphate by taking the time-average rates (i.e., the amount of persulphate decomposed at time t/time t, in m dm^{-3} s^{-1}) of persulphate decomposition. It is seen that the order decreased with time, and the extrapolated order at zero time was 1.20 (Fig. 6). The agreement between the two values of the order of persulphate seems to be satisfactory.

Figure 7 shows the pH change with time during the reaction in the presence and absence of monomer; the pH of the persulphate solution decreased rapidly initially, and then slowly with time. Increase of MAN concentration in the solution reduced the rate at which pH decreased, but the pH change (i.e., ΔpH) was not zero in this system, even when the solution was saturated with monomer (3.5%, v/v, at 50°C), whereas ΔpH was almost zero in the persulphate–acrylonitrile system[7] containing 8.5% acrylonitrile (w/v).

Figure 8 shows the effect of injected monomer late in a run on the rates of persulphate decompositions. It is found that the injected monomer late in a run accelerated the rates of persulphate decompositions. This clearly indicates that the monomer in the aqueous phase is interacting with the $S_2O_8^{2-}$ ions.

Table I shows the conversion of monomer to polymer with time in the aqueous polymerization of MAN. The number average molecular weights (M_n) of the polymer was of the order of 10^5.
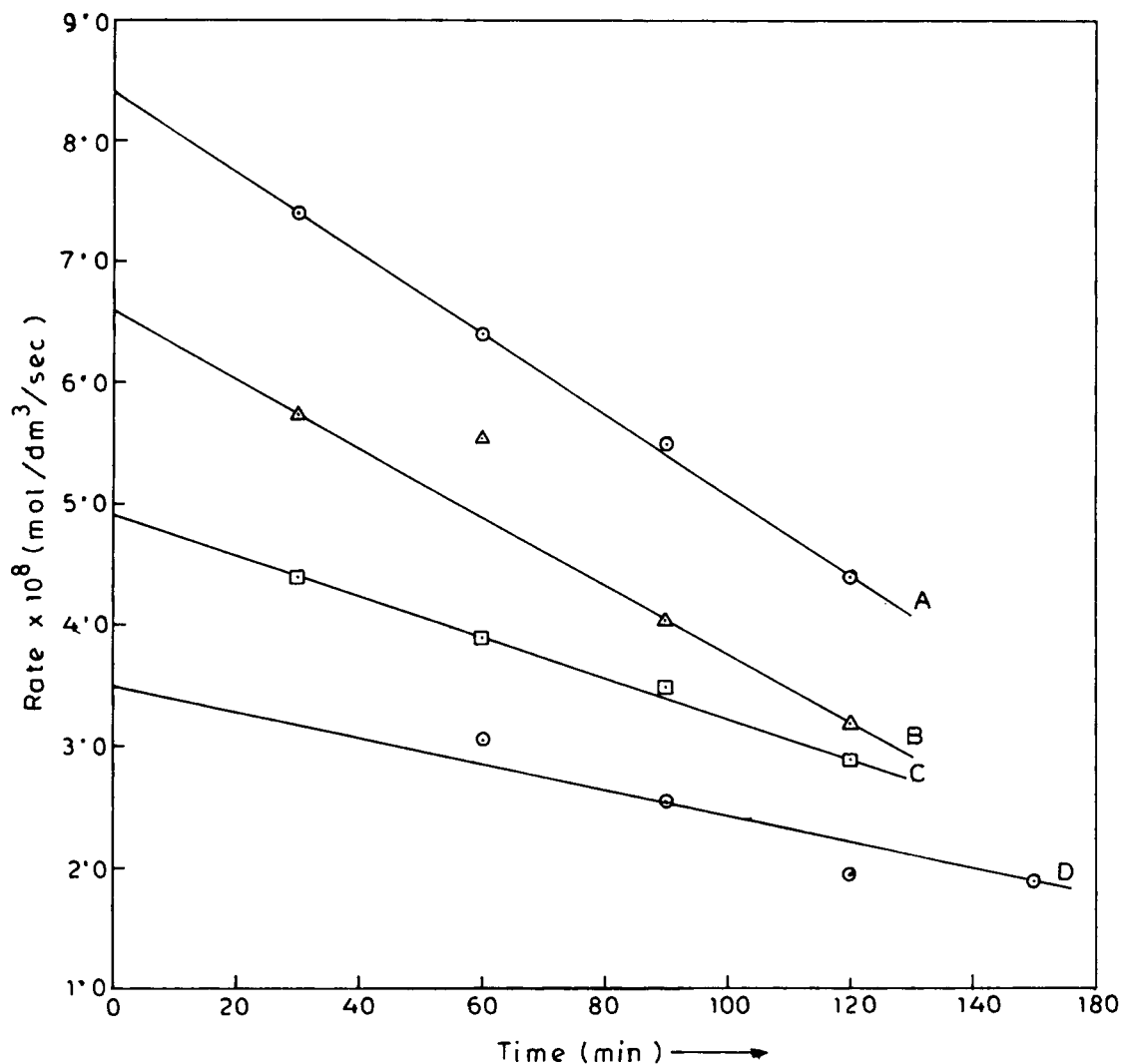
The Huggins' constant (K_H) in dimethylformamide solvent was found to be 0.366 at 30°C. The latex particles were found to be unstable in the presence of higher concentrations of persulphate (above 1.0×10^{-2}, m/dm³).

DISCUSSION

The data presented here show clearly that the initial rates of persulphate decomposition are a function of monomer concentration as well as of the initiator concentrations in the aqueous phase. The simple mechanism of persulphate decomposition in the presence of a vinyl monomer, stated in the introduction, predicts that the rate of persulphate decomposition would be independent of monomer concentrations, and so this mechanism is not con-
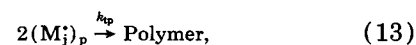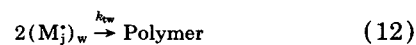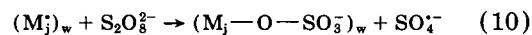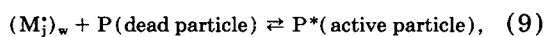
Table I   Molecular Weights and Colloidal Stability of Polymers in the Latex Solution

Time (min)	% Conversion of Monomer to Polymer	Colloidal Stability (mm MgSO₄ per dm³)	$(\eta) \times 10^{-2}$ (mL/g)	$(M_n) \times 10^{-5}$
60	8.00	36.60	—	—
75	11.13	32.60	2.39	5.63
105	16.97	—	2.74	7.40
120	19.55	—	2.75	7.47
135	22.14	—	2.75	7.47
150	24.30	—	—	—
165	26.47	29.80	2.67	7.02

Figure 3   Determination of initial rates of persulphate decompositions at a given concentration of persulphate (0.75×10^{-2} m/dm^3) and at various concentrations of MAN. A, 0.36; B, 0.30; C, 0.24; and D, 0.18 m/dm^3. The extrapolated rates at zero time are the initial rates.

sistent with our experimental results. The following elementary reactions are found to explain our experimental observations:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-} \tag{1}$$

$$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^- + \dot{O}H \tag{2}$$

$$2OH \rightarrow H_2O_2 \ (\text{or } H_2O + \tfrac{1}{2}O_2) \tag{3}$$

$$SO_4^{\cdot-} + M \rightarrow M_1^{\cdot}(=^-O_3S\!-\!O\!-\!M^{\cdot}), \tag{4}$$

$$SO_4^{\cdot-} + M(RH) \rightarrow HSO_4^- + R^{\cdot} \tag{4a}$$

$$S_2O_8^{2-} + M \rightarrow M_1^{\cdot} + SO_4^{\cdot-} \tag{5}$$

$$M_j^{\cdot} + M(=RH) \rightarrow M_jH + R^{\cdot} \tag{6}$$

$$M_j^{\cdot} + M \xrightarrow{k_p} M_{j+1}^{\cdot} \tag{7}$$

$$(M_j^{\cdot})_w \rightleftarrows (M_j^{\cdot})_p \tag{8}$$

$$(M_j^{\cdot})_w + P(\text{dead particle}) \rightleftarrows P^*(\text{active particle}), \tag{9}$$

$$(M_j^{\cdot})_w + S_2O_8^{2-} \rightarrow (M_j\!-\!O\!-\!SO_3^-)_w + SO_4^{\cdot-} \tag{10}$$

$$(M)_w \rightleftarrows (M)_p \tag{11}$$

$$2(M_j^{\cdot})_w \xrightarrow{k_{tw}} \text{Polymer} \tag{12}$$

$$2(M_j^{\cdot})_p \xrightarrow{k_{tp}} \text{Polymer}, \tag{13}$$
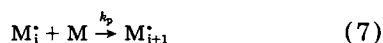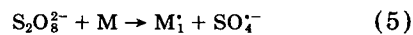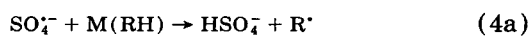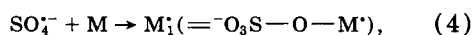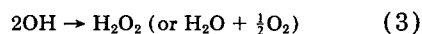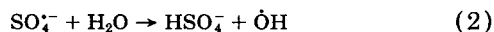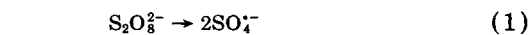
In the absence of monomer, $SO_4^{\cdot-}$ primary free radicals are produced only in reaction (1) and would disappear via reaction (2), and so the solution would be acidic, pH of the solution would decrease with time, which is consistent with the results shown in
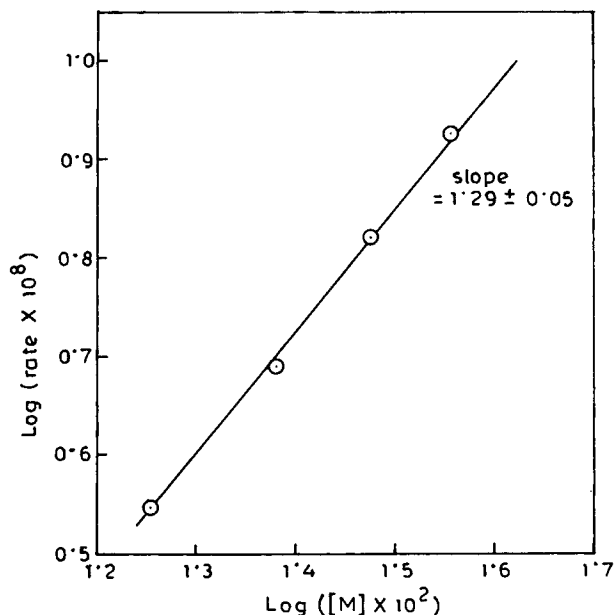
Figure 4 Order plot for the monomer from the equation: $-d(S_2O_8^{2-})/dt \propto (M)^x$. The slope of the line obtained by plotting $\log(\text{rate})$ vs. $\log(M)$ gives the value of (x) as 1.29 × 0.05.

Figure 7. In the presence of monomer, $SO_4^{\cdot-}$ radicals are also produced via reactions (5) and (10), and disappear via (2), (4), and (4a). If the monomer is highly reactive toward $SO_4^{\cdot-}$ radicals, and where $SO_4^{\cdot-}$ addition to the olefinic double bond of the monomer is not hindered due to the steric effect of the adjacent alkyl groups viz. CH_3, C_2H_5, C_6H_5, etc., then almost all the $SO_4^{\cdot-}$ radicals would disappear via (4), as was found in the persulphate–acrylonitrile system.[7] In the latter system, the pH of the medium did not alter when the aqueous solution was saturated with the monomer.[7] In the MAN–persulphate system, however, it is found that there was slight pH change even when the aqueous solution was saturated with MAN (Fig. 7). This indicates that either reaction (2) or (4a) or both were occurring even when the solution was saturated with methacrylonitrile. It seems to us that because of the steric effect of the CH_3 group in MAN (i.e., $CH_2{=}C(CH_3)CN$) a fraction of the $SO_4^{\cdot-}$ radicals would disappear via (4a), and this would probably account for the decrease of pH with the time even when the aqueous solution was saturated with MAN.

From the data shown in Figure 1, the first-order rate constant (k_1) of the reactions (1), viz: $S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-}$, was found to be 1.71×10^{-6} sec^{-1}, which agrees with the literature values[4] viz.: (1.3–2.61) × 10^{-6} sec^{-1} at 50°C. In our measurements, we found that k_1 was independent of pH in the range
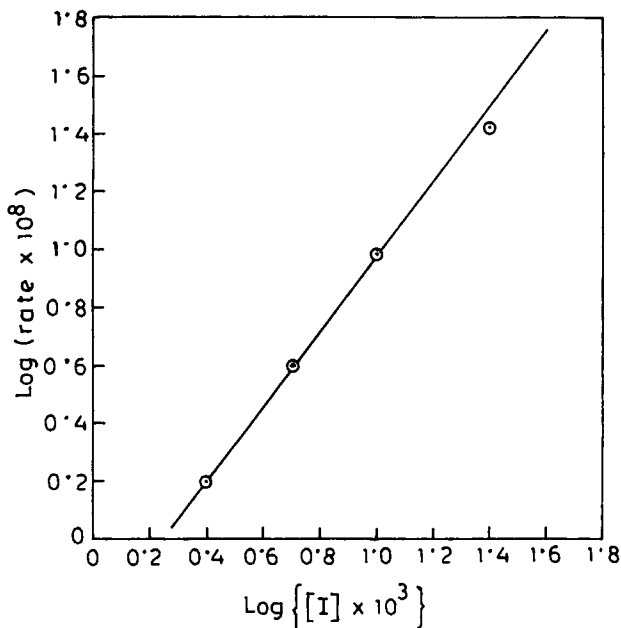
Figure 5(a) Order plot of the persulphate with respect to its decomposition in the presence of monomer. Log(initial rate of persulphate decomposition, in mol/dm^3/s) vs. log(persulphate initial concentration, in mol/dm^3) has been plotted. The slope of the line, 1.23, gives order of persulphate.
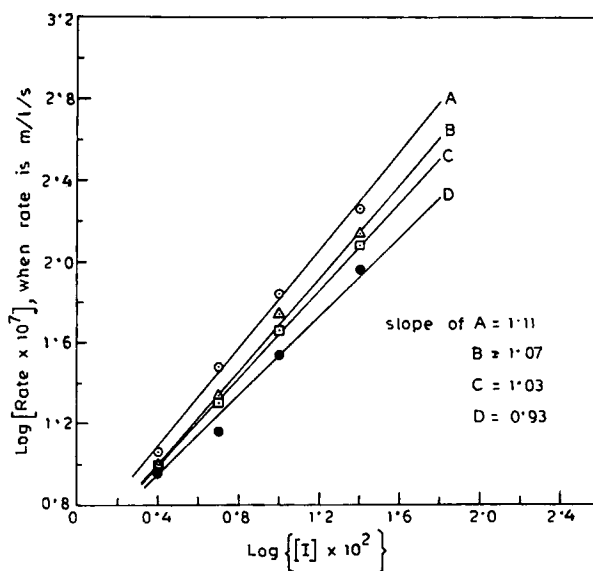
Figure 5(b) Estimation of order of persulphate with respect to its decomposition in the presence of monomer from the time-average rates of persulphate decomposition. A, rates at t = 60 min; B, rates at t = 90 min; C, rates at t = 120 min; D, rates at t = 180 min. The slopes of the lines are: A, 1.11; B, 1.07; C, 1.03; D, 0.93.
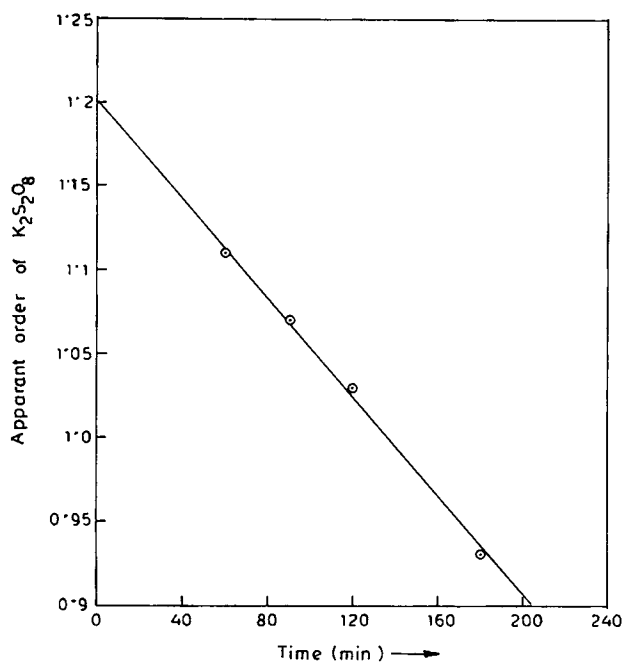
Figure 6 The apparent order of persulphate at various times from Figure 5(b) have been plotted as a function of time. The order at zero time is found to be about 1.20.

4–7, while Kolthoff et al.[1] and Wilmarth et al.[5] reported that k_1 was almost independent of pH in the range 3–13. Below 3 and above 13, k_1 was found to increase rapidly at a given temperature.[4,5,13] Only Breuer and Jenkins[14] reported that k_1 was pH dependent, and the maximum value of k_1 (= 2.82 $\times 10^{-6}$ sec^{-1}) was observed at pH 7 at 50°C. Such a high value of k_1 was not reported by any other worker.[3-5] Since the monomer order is not zero with respect to persulphate decomposition, it seems that there are other reactions that would account for the higher rates of persulphate decomposition in the presence of the monomer.

The most plausible reactions seem to be reactions (5) and (10), in which $S_2O_8^{2-}$ ions interact with the monomer directly and also with the water-soluble monomeric free radicals viz. $M_1^{\bullet}$ ($=^-O_3S$—O—CH_2—$\dot{C}(CH_3)$—CN) and R$^{\bullet}$ ($\equiv CH_2$=C—CN) or $\dot{C}H_2$—C—CN, which are resonating structures. For simple kinetic treatment, it is assumed that $M_1^{\bullet}$ and R$^{\bullet}$ are indistinguishable. It follows from the proposed mechanism that
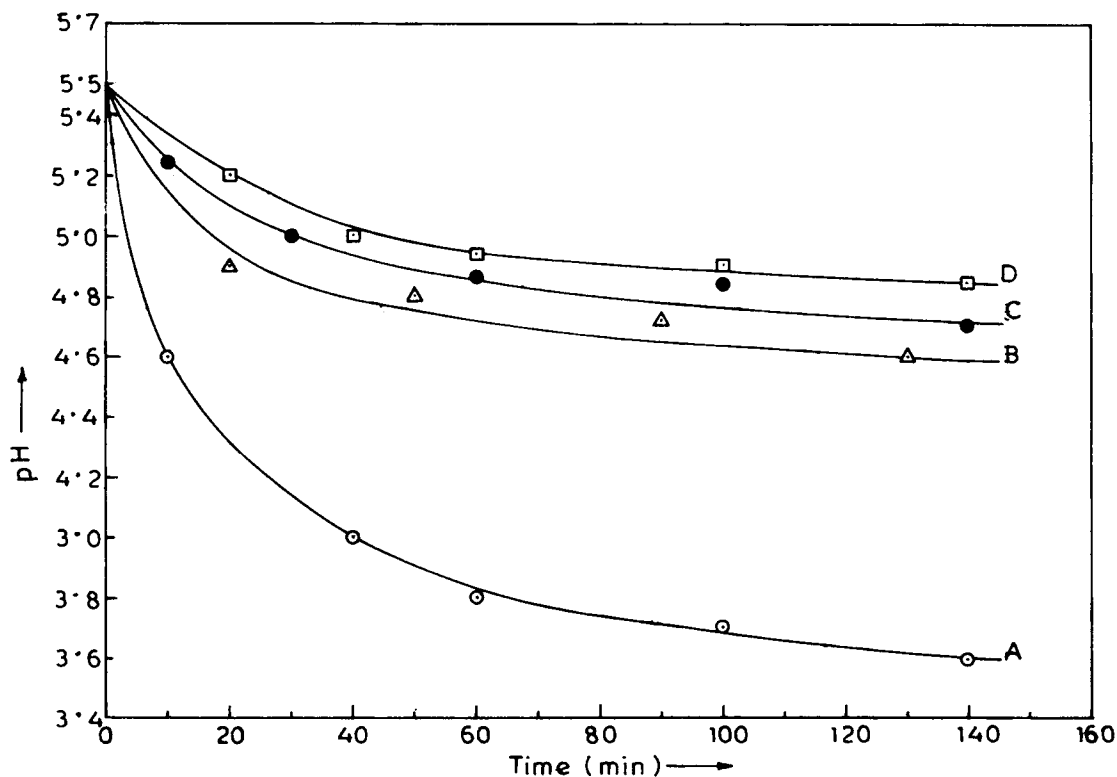
Figure 7 Effect of monomer concentrations on the pH change of the aqueous solutions of persulphate (10^{-2}, m/dm^3) during its decomposition at 50°C. pH was measured at 25°C. A, persulphate alone; B, persulphate and monomer (0.06, m/dm^3); C, persulphate and monomer (0.18 m/dm^3); D, persulphate and monomer (0.42 m/dm^3).
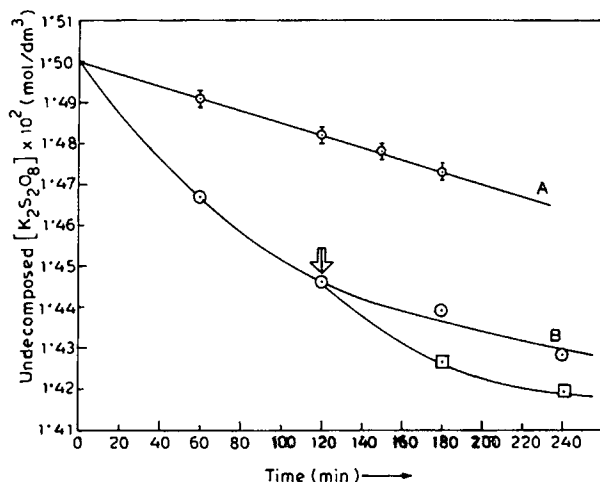
Figure 8 Effect of monomer, when injected late in a run, on the decompositions of persulphate (KPS). Curve A, KPS = 1.50×10^{-2} (m/dm^3); Curve B, KPS = 1.50×10^{-2} (m/dm^3) and MAN = 0.30 (m/dm^3). Additional quantity of MAN (0.12 m/dm^3) was injected at the 120th minute. The arrow indicates the point of injection. The injected monomer accelerated the rates of decomposition ($\square$).

$$\frac{-d(S_2O_8^{2-})}{dt} = k_1(S_2O_8^{2-}) + k_5(S_2O_8^{2-})(M)$$

$$+ k_{10}(M_j^{\bullet})_w(S_2O_8^{2-}). \quad (1)$$

Rate of initiation in the aqueous phase $(R_i)_w$, is given by

$$(R_i)_w = [2k_1(S_2O_8^{2-}) + 2k_5(M)(S_2O_8^{2-})$$

$$+ k_{10}(M_j^{\bullet})_w(S_2O_8^{2-})]V_w, \quad (2)$$

where V_w is the volume fraction of water. V_p is the volume fraction of polymer, so that $V_w + V_p = 1.0$. Assuming (1) and (5) are major chain-initiating reactions, and neglecting (10), we get

$$(R_i)_w = [2k_1 + 2k_5(M)](S_2O_8^{2-})V_w. \quad (3)$$

Under our experimental conditions, $V_w \gg V_p$ and so here $V_w \simeq 1.0$. Rate of termination in the aqueous phase, $(R_t)_w$, is given by

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

In the steady state, $(R_i)_w = (R_t)_w$; hence,

$$(M_j^{\bullet})_w = k_{tw}^{-1/2}[k_1 + k_5(M)]^{1/2}(S_2O_8^{2-})^{1/2}. \quad (5)$$

Combining (1) and (5), we get

$$\frac{1}{(S_2O_8^{2-})}\left[\frac{-d(S_2O_8^{2-})}{dt}\right] = \{k_1 + k_5(M)\}$$

$$+ k_{10}k_{tw}^{-1/2}[k_1 + k_5(M)]^{1/2}(S_2O_8^{2-})^{1/2}. \quad (6)$$

It follows from eq. (6) that at a given monomer concentration a plot of LHS vs. $(S_2O_8^{2-})^{1/2}$ would give a straight line, which is consistent with the results shown in Figure 9. From the slope and the intercept of the line, k_5 and k_{10} have been estimated, taking $k_1 = 1.71 \times 10^{-6}$ sec^{-1}, $k_{tw} = 7.32 \times 10^9$ (dm^3 m^{-1} s^{-1}) from Dainton et al.[15] for the aqueous polymerization of acrylonitrile, since k_{tw} for the aqueous polymerization of MAN is not known. The monomer concentration was 0.36 (m/dm^3), and k_5 was found as 1.05×10^{-5} (dm^3 m^{-1} s^{-1}), and k_{10} as 1.14×10^3 (dm^3 m^{-1} s^{-1}). It may be pointed out here that Dainton's k_p and k_t for the aqueous polymerization of acrylonitrile have been questioned by McCarthy et al.,[16] who believe that Dainton's k_p and k_t values were very high.

Figure 8 shows that when MAN was injected late in a run the rate of persulphate decomposition was again accelerated. This shows clearly that the monomer in the aqueous phase is responsible for the accelerated rate of persulphate decomposition. Since in a given run the rate of persulphate decomposition was found to decrease continuously with time (Fig. 1) or with the conversion of monomer to polymer, it is clear that the polymer in the latex particles was not responsible for the induced decomposition of persulphate in this system. Further, the polymer was found to be soluble in N-N-dimethyl formamide solvent, and it indicates that no crosslinked polymer was formed during the reac-
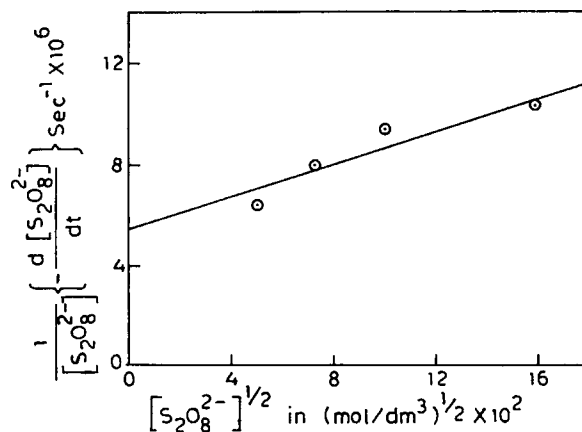
Figure 9 Plot of $(I)^{-1} \times (-d(I)/dt)$ vs. $(I)^{0.5}$ at a given concentration of the monomer, as shown in eq. (6); here $(I) = (S_2O_8^{2-})$.

tions. In the vinyl acetate—persulphate and methyl acrylate–persulphate systems, it was observed[17] that the injected monomer late in a run had no measurable effect on the rates of persulphate decomposition. It is believed that these monomers are good solvents for their respective polymers, and so they are quickly absorbed by the existing latex particles in the system, and very little of the injected monomer remains in the aqueous phase. For MAN, the distribution coefficient (i.e., concentration of monomer in the polymer phase/concentration of monomer in the aqueous phase at 50°C) is very low (about 0.50), whereas that of vinyl acetate or methyl acrylate is very high,[17] viz. about 22.0 ± 2.0.

The data of Table I show that the rate of polymerization is very slow and the total conversion in 165 min is also very small, viz. only about 26%. It seems that the locus of polymerization shifted overwhelmingly from the aqueous phase to the surface of the latex particles, where polymerization occurred at a slow rate due to the relatively low concentration of monomer at the reaction site. The polymerization, however, occurred at an accelerated rate. The colloidal stability of the latex particles was found to decrease with time, which indicates that incipient coagulation of the latex particles was taking place during the reactions. Molecular weights of the polymer were found to increase with time at the early stages of the reaction, attain a maximum, and then fall with time. This observation is probably associated with the change of polymerization rates with time. Similar observations were noted in the emulsion polymerization of styrene[18] and also in the aqueous and emulsion polymerizations of methyl acrylate[19] and of ethyl acrylate.[6]

The effect of ionic strength on the value of k_1 is controversial. We have found that K_2SO_4 (10^{-3}–10^{-4}, m/dm^3) has no measurable effect on the value of k_1 (1.71 ± 0.05) × 10^{-6} sec^{-1} at 50°C. Kolthoff and Miller[20] reported that sodium perchlorate had no effect on the rate of persulphate decomposition under conditions almost identical to those of Singh and Venkatarao,[13] who reported that the rate of persulphate decomposition decreased with the increase of concentration of sodium perchlorate. Pethybridge and Prue[21] stated specific ion effects on the reactions of persulphate. It seems that the impurities (in traces) present in the reagents were responsible for the controversies.[4]

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