

# The Decomposition of Sodium Persulfate in the Presence of Acrylic Acid

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**ABSTRACT:** The activation energy and rate constants for the decomposition of sodium persulfate in the presence of acrylic acid have been determined for monomer compositions representative of those used in a polymerization process to prepare sodium polyacrylate superabsorbent polymers. It was found that, relative to buffered aqueous conditions, the rate of decomposition of sodium persulfate is increased by a factor of two- to sevenfold in the presence of acrylic acid, low levels of neutralized acrylic acid, or high levels of acrylic acid at low % neutralization, due to an induced decomposition mechanism by the monomer. However, high concentrations of partially neutralized acrylic acid (high solids) decrease the decomposition rate of persulfate relative to that in the presence of acrylic acid (not neutralized). An ionic gel cage mechanism that influences the rate of decomposition of sodium persulfate is proposed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 591–600, 1997

**Key words:** kinetics; sodium persulfate; decomposition; acrylic acid; superabsorbent

## INTRODUCTION

Sodium persulfate is used as a polymerization initiator in a variety of processes, including those to make acrylic and styrene–butadiene latexes, emulsion acrylonitrile–butadiene–styrene plastics, and polyacrylic acid-based superabsorbent resins. Kolthoff and Miller<sup>1</sup> determined that persulfate decomposed by two different mechanisms depending on the pH and temperature of the solution. At a pH < 2, an acid catalyzed, nonfree radical route leading to sulfur tetroxide and bisulfate dominates. In dilute acid solutions, the sulfur tetroxide decomposes to sulfuric acid and oxygen. At a pH > 4, persulfate decomposes by homolytic cleavage to generate two sulfate ion radicals with an activation energy of 33.5 kcal/mol. The acid-

catalyzed reaction results in a loss of persulfate by a process that does not generate free radicals and does not contribute to the polymerization reaction. It is a fast reaction and if not buffered, further accelerates the acid catalyzed decomposition as the sulfuric acid that is generated further increases the acidity. Between a pH of 4 and 13, the thermal decomposition rate varies only by a factor of 2, with the maximum rate occurring at a pH of about 7.<sup>2</sup>

The rates of decomposition of peroxide and other polymerization initiators have been found to be significantly enhanced in the presence of reactive monomers or other species such as soaps and certain oxidizable species. Morris and Parts have reported up to a 50-fold increase in the rate of decomposition of potassium persulfate in the presence of monomers such as vinyl acetate.<sup>3</sup> The rate of decomposition of persulfate is also affected by the concentration of these reactive species, gen-

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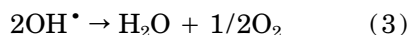
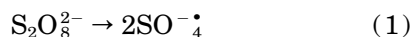
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erally up to a limiting concentration, above which no additional effect is observed.

In the presence of reactive or oxidizable species, the disappearance of persulfate has been observed<sup>4</sup> to depend on greater than the first power of the initial persulfate concentration and frequently to have both an initial fast decomposition rate and then a slower rate later in the reaction.<sup>3</sup>

Initiators can even react with the solvent, depending upon the nature of the initiator and solvent. Bartlett and Cotman<sup>5</sup> have reported the reaction of potassium persulfate with methanol in an aqueous methanol solution. In a one molar solution of methanol in water at 80°C, persulfate decomposed 25 times faster than in buffered water. The methanol was oxidized to formaldehyde and the reaction order was 3/2 in persulfate. This was similar to the 3/2 reaction order seen for persulfate decomposition during the polymerization of allyl alcohol.<sup>3</sup> In water, the decomposition of persulfate was first order, as one would expect when induced decomposition and other radical reactions did not influence it.<sup>6</sup>

The fate of the radicals produced from persulfate decomposition in water has been studied and reactions between water and the sulfate ion radical occur. The overall mechanism can be written as follows:



Using <sup>18</sup>O-labeled water, Kolthoff and Miller found that the source of the oxygen in the liberated O<sub>2</sub> was from the water and not the persulfate in neutral and basic solutions.<sup>1</sup> Polymer end group analysis has shown that when monomers are present, the polymerization is generally initiated by the sulfate ion radical and not OH radicals.<sup>6</sup> This shows that the monomers are efficient at intercepting the sulfate ion radical before the radicals react with water.

Conflicting conclusions have been reached concerning the influence of ionic strength on the rate of persulfate decomposition. Kolthoff and Miller<sup>1</sup> concluded that a salt such as sodium perchlorate does not influence the rate of persulfate decomposition while others<sup>7</sup> have reported a decrease in decomposition rate with increasing ionic strength. In neutral and slightly basic solutions, it appears that ionic strength has only a slight influence on the decomposition rate of persulfate and many of

the differences reported in the literature are the result of trace impurities and surface effects.<sup>2</sup>

The decomposition rate can be quantified by direct measurement of the disappearance of the reactive species. However, because the initiator is frequently present at very low concentrations and difficult to detect directly, indirect methods have been used in the past. Colorimetric methods have been used to determine the rate of decomposition of benzoyl peroxide and 2,2'-azo-bis(isobutyronitrile), AIBN.<sup>8</sup> The highly colored  $\alpha,\alpha$ -diphenyl  $\beta$ -picryl hydrazyl radical reacts with the radicals generated by the decomposition of the initiators, and the rate of decrease in color is directly proportional to the initiator decomposition rate.

Other indirect methods used to quantify persulfate, such as the back-titration of Fe<sup>3+</sup> from the persulfate oxidation of added Fe<sup>2+</sup>, are nonspecific and are affected by other oxidizing species and oxygen.<sup>9</sup> Anion exchange liquid chromatography with ultraviolet detection has been used for direct determination of persulfate in some systems,<sup>10</sup> but ultraviolet-absorbing species such as acrylic acid mask the response in polyacrylic acid superabsorbent resins. Polarography has also been used to directly quantify persulfate in latex and acrylic resins<sup>11</sup> but the utility of the direct approach for polyacrylic acid superabsorbent resins is limited because of matrix interferences, which give anodic response at the mercury electrode or suppress the polarographic reduction current resulting in a high detection limit for persulfate. By combining anion exchange chromatography with reductive electrochemical detection, persulfate can be directly and selectively determined in acrylic resins.

In the thermal decomposition of persulfate, the reaction kinetics are, in theory, first order and the rate of disappearance of persulfate,  $-d[I]/dt$ , is given by the expression

$$-d[I]/dt = k_d[I] \quad (4)$$

and the concentration at any time,  $t$ , can be calculated from the equation

$$\ln([I]_0/[I]) = k_d t \quad (5)$$

where  $[I]$  is the concentration of persulfate at time,  $t$ ,  $[I]_0$  is the initial persulfate concentration, and  $k_d$  is the rate constant for decomposition at the reaction temperature.

Because the rate of polymerization of acrylic acid,  $R_p$ , is directly proportional to the square root

of the rate constant for decomposition of the initiator,  $k_d$ , by the expression

$$R_p = k_p[M]^n \left( \frac{fk_d[I]}{k_t} \right)^{0.5} \quad (6)$$

it is important to have accurate decomposition rate data under conditions of polymerization.

Properties of the superabsorbent and extractable levels in the final product are also influenced by the backbone molecular weight,  $M_n$ , which is related to  $k_d$  by the expression

$$M_n = \frac{k_p[M]^n}{(fk_d k_t[I])^{1/2}} \quad (7)$$

assuming termination by mutual coupling of the growing polymer radicals, where  $k_p$  is the propagation rate constant,  $[M]$  is the monomer concentration,  $f$  is the efficiency factor for the initiator,  $k_t$  is the termination rate constant, and  $[I]$  is the initiator concentration. If disproportionation of the growing polymer chains is the mechanism of termination, then the molecular weight is proportional to the reciprocal of the decomposition rate constant raised to the first power.<sup>12</sup> Therefore, a better quantification of the rate of persulfate decomposition in the presence of acrylic acid was needed for both process and property modeling.

## EXPERIMENTAL

### Preparation of Acrylic Acid Feed Mixtures

Key variables that might affect the thermal rate of decomposition of sodium persulfate in the presence of monomers were evaluated. These included pH (% neutralization), % solids, and temperature. Solutions of varying pH (% neutralization and % solids) were prepared in 8-ounce bottles. A typical preparation is exemplified by the following example. A stock solution of sodium persulfate was prepared by dissolving 0.450 g of sodium persulfate (Aldrich, 98+%) in 698.8 g of deionized (DI) water. Into an 8-ounce screw cap bottle, containing a Teflon-coated stirring bar, was weighed 28.12 g of glacial acrylic acid and 69.925 g of the sodium persulfate stock solution. To the stirred solution was added slowly, 13.456 g of sodium carbonate (Fisher, certified A.C.S.).

Additional samples were prepared by varying the ratio of the four components. The % neutral-

ization (pH) was varied by changing the amount of sodium carbonate added and the % solids was varied by diluting the reaction mixture with larger quantities of a persulfate stock solution (0.213 g of sodium persulfate and 499.79 g of DI water) to maintain an approximately constant molar sodium persulfate concentration. The initial concentration of sodium persulfate was maintained approximately constant at about 400 ppm, based on sample weight.

### Ampoule Polymerizations

In order to control the highly exothermic acrylic acid reaction and maintain isothermal conditions for obtaining decomposition data, capillary tube ampoules were prepared and used. The ampoules were prepared from 23-cm glass Pasteur pipettes. The tip was cut and sealed to provide a capillary section that was 10 cm long and 1.6 mm (o.d.) in diameter. The high surface-to-volume ratio of these ampoules provided good heat transfer for the reactions. The ampoules were rinsed with acetone, followed by a DI water rinse, and dried before use. Each batch of ampoules was rinsed twice with the feed mixture immediately before loading. An amount of the acrylic acid solution was added to fill only the narrow (1.6 mm) section of the ampoule. The weight in each tube was recorded to later simplify the persulfate analysis. Deoxygenation of each ampoule was done by bubbling nitrogen through the samples. A hole was punched in the polyethylene cap and a capillary tube inserted through the hole to deliver nitrogen to the sample. The larger diameter, upper portion of the ampoule was necessary to allow the foam bubbles to break and drain back into the ampoule. Feed mixtures in narrow diameter, straight walled ampoules were blown out of the top by the nitrogen gas. Samples were deoxygenated 30–45 min by a steady stream of nitrogen being passed through the solution before sealing and placing in a temperature-controlled water bath. Samples were drawn over a 23-h period for reactions conducted at 55°C, 10 h when run at 70°C, and over a 2-h period for 85°C conditions.

### Sample Analysis

The preweighed polymerized samples in 1.6-mm capillary tubes were stored in a freezer as they were taken and then placed on ice until analysis (about 4 h). Each tube was placed in 500 mL glass bottles, fractured, and a known volume of 5% (w/w)  $\text{Na}_2\text{SO}_4$  solution (15–100 mL) was added. The

mixture was homogenized using a mechanical blender and the solution was allowed to stand for 10 min. An aliquot was filtered through glass wool and a 0.45  $\mu\text{m}$  nylon-66 syringe filter. A known volume of saturated bromine water was added to the aliquot until the solution remained amber for 1 min. Then a known volume of sodium formate (10% w) was added until the amber color disappeared. The solution was transferred to an autoinjector vial and deoxygenated prior to injection into the chromatograph. Injection of the prepared solution was carried out in duplicate.

For 0% neutralized samples, the mechanical blender was not used for sample homogenization because of persulfate loss during the preparation step. It appeared as though trace metals leached from the mechanical blender under the acid conditions, which then catalyzed the decomposition of the sodium persulfate. Consequently, these samples were shaken for 10 min using a bed shaker (or by hand) and then prepared as above.

Sodium persulfate was determined by anion exchange chromatography using reductive electrochemical detection. The analytical column was 250  $\times$  3.0 mm i.d. and contained quaternary ammonium latex anion exchanger (6250 Å) on 10–20  $\mu\text{m}$  surface-sulfonated styrene divinylbenzene substrate. The column was protected by a 50  $\times$  3.0 mm i.d. guard column of the same material. The mobile phase was 0.07M NaClO<sub>4</sub> continuously purged with water-saturated prepurified helium to remove oxygen and the flow rate was 1.4 mL/min. The injection volume was 100  $\mu\text{L}$ . The detector was a model 310 static mercury drop electrode with a model 174A potentiostat (EG&G Princeton Applied Research). The drop size was large, the drop time, 1.0 s; mode, sampled DC; and applied potential, –0.300 V vs. Ag/AgCl (1M LiCl).

Sample deoxygenation was accomplished using a model 231/401 autosampling injector equipped with a model 401 diluter/pipetter and a sampler controller keypad (Gilson Medical Electronics, Middleton, WI). The unit was modified by replacing all plastic tubing with oxygen-impermeable PEEK tubing. A model 401A pneumatically actuated switching valve and a model 201 solenoid interface (Autochrom Inc., Milford, MA) were used to automatically switch the system between deoxygenation and sample aspiration/flush modes. Additional details have been reported by Theoharidies et al.<sup>13</sup>

### Sample Calculations

Sodium persulfate was quantified by external standard analysis using calibration factors deter-

mined from two-, three- or four-point calibration. Results were calculated according to:

$$\begin{aligned} & \mu\text{g/g Na}_2\text{S}_2\text{O}_8 \\ & = \text{Peak Area}/\text{RF} \times (\text{A} + \text{B} + \text{F})/\text{A} \times \text{S}/\text{W} \quad (8) \end{aligned}$$

where RF is a response factor determined from calibration, A is the volume (mL) of filtered aliquot taken for bromine treatment, B is the volume (mL) of saturated bromine water added to the aliquot, F is the volume (mL) of 10% sodium formate added to A + B, S is the volume (mL) of 5% Na<sub>2</sub>SO<sub>4</sub> added to the preweighed ampoule containing sample weight, W (grams). The mean of the duplicate injections was reported.

## RESULTS AND DISCUSSION

At a mercury electrode and at potentials negative of +0.50 V, persulfate is reduced according to:

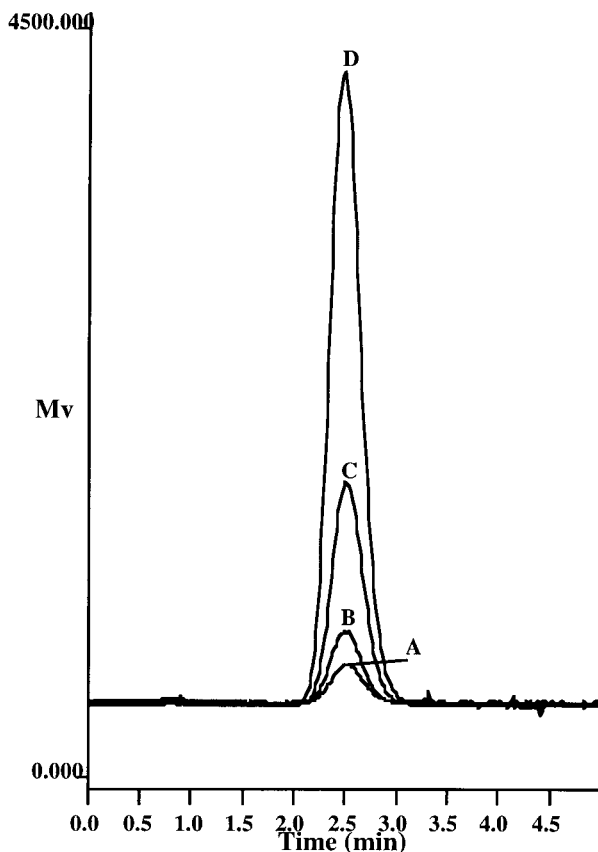


When applied to superabsorbent polymers (or media containing acrylic acid at high concentration), the specificity of the polarographic method suffers; however, when combined with ion exchange chromatography, electrochemical detection is a highly selective and sensitive method for the determination of persulfate in media containing superabsorbent polymers.

At potentials more negative than –0.10 V, dissolved oxygen (present at about 1 mM in aqueous solution) was electrochemically reduced. It was not a requirement of the analysis that sample deoxygenation be carried out; however, the run time was decreased from 10 to 5 min when oxygen was removed, thus allowing for faster sample throughput. The optimum time of sample deoxygenation was determined to be 3 min.

### Persulfate Determination in Acrylic Acid Polymers

Chromatograms showing typical response for sodium persulfate standards prepared in 5% (w) Na<sub>2</sub>SO<sub>4</sub> and deoxygenated for 3 min before injection



**Figure 1** Chromatograms showing response for sodium persulfate at various concentrations. (A) 3.72, (B) 7.43, (C) 22.3, (D) 55.75  $\mu\text{g/mL}$  sodium persulfate.

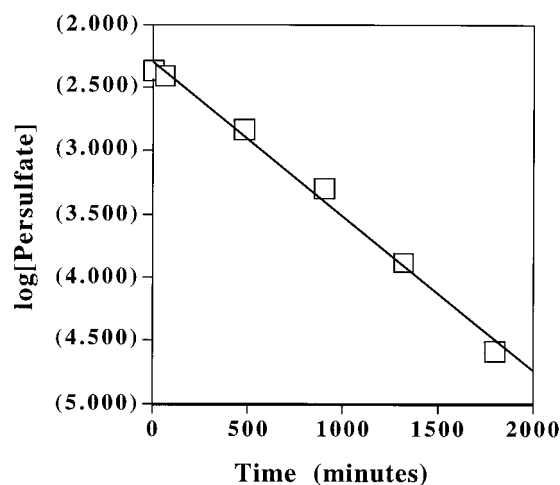
are given in Figure 1. Linear response was observed in the range 0.2–60  $\mu\text{g/mL}$ . The standard response was characterized by a retention time of 2.51 min and a system pressure of 13.8 MPa.

A complicating factor in quantifying the persulfate content was the very high level of acrylic acid in the samples. It was found that after only two injections of samples containing partially polymerized acrylic acid, the system pressure increased to >16.6 MPa and the peak retention time exceeded 5 min, indicating that acrylic acid was polymerizing on the guard or analytical column. A successful approach to eliminate on-column polymerization of acrylic acid was based on bromination chemistry. Acrylic acid was readily brominated at ambient temperature using bromine water. The excess bromine was then quenched by reaction with sodium formate. Brominated acrylic acid showed little tendency to polymerize on-column as evidenced by a pressure increase of only 0.7 MPa after >100 injections. Increasing concentrations of brominated acrylic acid did not ad-

versely affect recovery, but it did increase the persulfate retention time slightly. For this reason, all results were calculated using peak area.

Analysis precision was determined by analyzing the sample four times. The mean  $\text{Na}_2\text{S}_2\text{O}_8$  concentration was 237  $\mu\text{g/g}$  and the standard deviation was 4.6. Recovery of persulfate from a sample matrix was determined by fortifying the extract solution of a low conversion sample (20% conversion and containing 370  $\mu\text{g/g}$  of sodium persulfate) with 7.4  $\mu\text{g/mL}$  sodium persulfate and performing sample preparation and analysis. The recovery was 96.4%.

Preparation of unneutralized samples containing excess acrylic acid could not be carried out in the usual manner. It was observed that when these samples were prepared with the use of a metal mechanical homogenization device, the solutions gave off an odor of sulfide and took on a grayish color. Analysis showed low persulfate values, indicating a loss of persulfate due to acid or acid/metal catalyzed decomposition. Also, in contrast to neutralized samples, deoxygenation of these samples was plagued by foaming problems, which resulted in widely scattered data due to incomplete filling of the injection loop. When the samples were extracted by shaking with 5%  $\text{Na}_2\text{SO}_4$  for 10 min (without mechanical homogenization) no sulfide odor was detected. For 65% neutralized samples, the shaking extraction procedure and mechanical homogenization gave equivalent results. It should also be possible to preneutralize acid-containing samples with sodium carbonate or sodium hydroxide and carry out shaking extraction or mechanical homogeni-



**Figure 2** Decomposition rate data for sodium persulfate at 69.8°C in water containing 0.01M  $\text{NaHCO}_3$ .

**Table I Rate Constants Determined for Persulfate at 70°C in Buffered Water**

$k_d$ ( $\text{min}^{-1}$ )	Authors	Conditions
$1.4 \times 10^{-3}$ (@ 70.0°C)	Kolthoff and Miller <sup>1</sup>	0.01M potassium persulfate + 0.1M NaOH/0.1M HClO <sub>4</sub>
$2.8 \times 10^{-3}$ (@ 69.8°C)	This work	0.0042M sodium persulfate + 0.01M NaHCO <sub>3</sub>

zation without sample loss due to persulfate decomposition or solution foaming problems.

### Density Corrections

During the course of the polymerization of acrylic acid feed mixtures, there is a volume contraction. When reporting persulfate concentration in ppm based on acrylic acid, the changing volume poses no problem. However, kinetic parameters that are concentration dependent, such as first-order decomposition rates of initiators, require density corrections in order to report concentrations in moles/liter. In this work, the volume of the reaction mixtures was corrected based on conversion.

The rate constant for decomposition of sodium persulfate determined in buffered water (0.01M

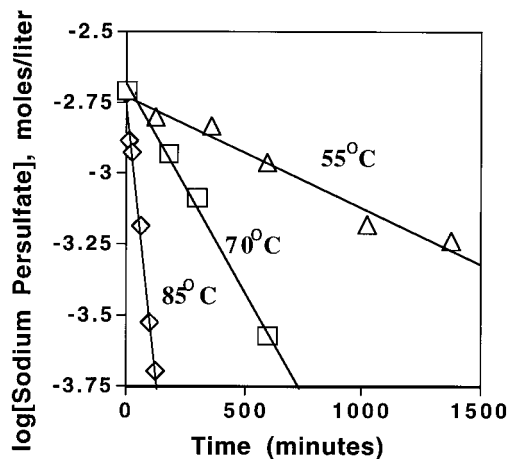
NaHCO<sub>3</sub>) at 69.8°C (Fig. 2) was compared to that determined previously for potassium persulfate at 70°C by Kolthoff and Miller.<sup>1</sup> Samples were prepared in a buffered system (0.01M NaHCO<sub>3</sub>) at the concentration of persulfate used in typical acrylic acid polymerization processes, in the absence of monomer, and ampoules were withdrawn from the water bath over a 30-h period. The decomposition rate constant calculated from these data compare favorably (Table I) with that reported by Kolthoff and Miller.<sup>1</sup>

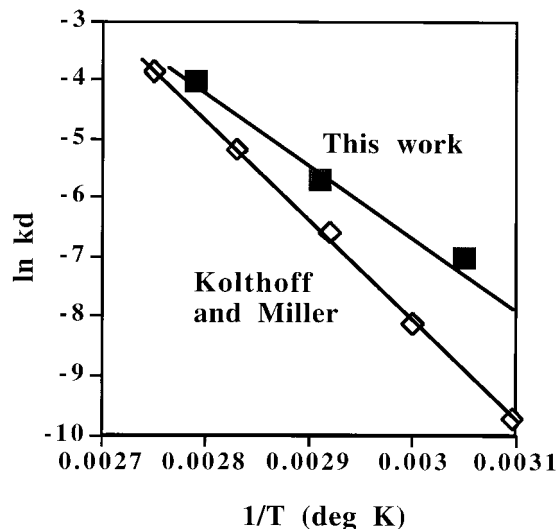
The decomposition rate data for sodium persulfate determined at 55, 70, and 85°C in the presence of 65% neutralized acrylic acid at 33.8% solids are presented in Table II. The concentration in mol/liter includes the correction for the density change that occurs upon polymerization. The first-order decomposition plots of log [persulfate] vs. time are shown in Figure 3. The data are consistent with the expected first-order decomposition mechanism. The rate of decomposition at 55°C is significantly faster than that in buffered aqueous systems and approaches the decomposi-

**Table II Decomposition Rate Data for Sodium Persulfate vs. Time at Various Temperatures in the Presence of 65% Neutralized Acrylic Acid at 33.8% Solids**

Time (min)	Temp (°C)	[Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] (ppm) <sup>a</sup>	[Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ] (mol/L)
0	55	420	0.00198
120	55	311	0.00158
360	55	289	0.00147
600	55	213	0.00108
1020	55	129	0.000657
1380	55	114	0.000581
0	70	421	0.00198
180	70	230	0.00117
300	70	160	0.000815
600	70	53	0.000270
0	85	408	0.00192
10	85	258	0.00131
20	85	234	0.00119
60	85	128	0.000652
100	85	59	0.000301
120	85	40	0.000204

<sup>a</sup> Based on total sample weight.

**Figure 3** First-order decomposition plots for sodium persulfate at 55, 70, and 85°C in the presence of 65% neutralized acrylic acid.



**Figure 4** Effect of temperature on the persulfate decomposition rate constant in buffered water and in the presence of 65% neutralized acrylic acid at 33.8% solids.

tion rate of the aqueous systems at higher temperatures. The higher rates of persulfate decomposition observed in this study, especially at the lower temperatures, may be the result of induced decomposition. Induced decomposition would be expected to have a greater influence on the rate at lower temperatures, consistent with the observations. The monomer is a likely specie causing the increased decomposition rate as observed in other systems containing polymerizable monomers. In commercial polymer production equipment, another factor that could accelerate the decomposition rate is trace metals, especially from stainless steel agitators and internal reactor baffles or flaws in glass-lined reactors. Glass was used for all samples in the present study. It is generally assumed that sodium persulfate is relatively stable at room temperature; however, it has been found that persulfate in swollen polyacrylic acid gel samples decomposes quite rapidly, even in a

freezer (ca. 50% loss in 2 weeks), providing additional support for low temperature-induced decomposition mechanisms.

The activation energy for the decomposition of persulfate was determined by plotting the natural log of the rate constants vs. the reciprocal of the temperature (K) from the Arrhenius equation,  $k_d = A_p^* e^{-E_a/RT}$ , as shown in Figure 4. The data of Kolthoff and Miller<sup>1</sup> for the decomposition of potassium persulfate in buffered water is shown for comparison. The data of Kolthoff and Miller are frequently used for kinetic purposes when persulfate is used in a process. The activation energy,  $E_a$ , and collision frequency factor,  $A_p$ , are quite different for persulfate in the presence of acrylic acid or partially neutralized acrylic acid, than in buffered water (Table III). The activation energy of 22.6 kcal/mol is quite low and indicates that the rate of decomposition in the acrylic acid feed mixture is less temperature sensitive than in aqueous solutions.

The effect of monomer content (% solids) on the rate of decomposition of sodium persulfate was quite surprising. We expected to observe an increased rate of decomposition in the presence of the monomer, which we did and which was quite significant at low levels (3.4%) of neutralized acrylic acid (Table IV and Fig. 5). However, higher levels of monomer (16.9 and 33.8% solids), resulted in a decrease in the rate of decomposition by a factor of three compared to the rate at the lower monomer content. It is speculated that low levels of monomer increase the rate of decomposition by intercepting the radicals as they are formed in the solvated cage, thus preventing recombination back to persulfate. At higher solids content, mobility of the charged sodium acrylate is reduced,<sup>14</sup> which could reduce the rate of entrance of the monomer into the ionized gel cage surrounding an initiator molecule, resulting in less induced decomposition of the persulfate. An-

**Table III** Activation Energy and Collision Frequency Factor for Persulfate Decomposition

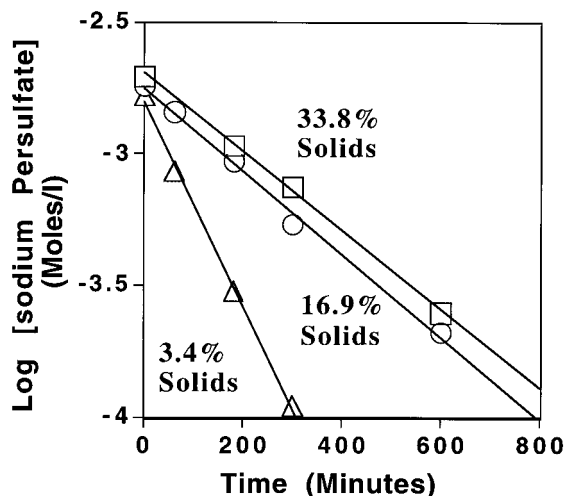
	$E_a$ (kcal/mol)	$A_p$ (min <sup>-1</sup> )	Reference
Potassium persulfate in buffered water	33.5	$4.0 \times 10^{18}$	Kolthoff and Miller <sup>1</sup>
Sodium persulfate in 65% neutralized acrylic acid solution at 33.8% solids	22.6	$8.6 \times 10^{11}$	this work

**Table IV Rate of Decomposition of Sodium Persulfate at 70°C in the Presence of 65% Neutralized Acrylic Acid at Various Monomer Contents**

Solids (%)	Time (h)	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (ppm)	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (mol/L)
3.4	0	391	0.00166
3.4	1	203	0.000870
3.4	3	71	0.000304
3.4	5	26	0.000111
16.9	0	399	0.00178
16.9	1	320	0.00149
16.9	3	209	0.000971
16.9	5	120	0.000557
16.9	10	46	0.000214
33.8	0	421	0.00198
33.8	3	230	0.00117
33.8	5	160	0.000815
33.8	10	53	0.000270

other contributing factor could be the reduced mobility in the ionized gel of the charged ion radical products formed by the homolytic cleavage reaction. If the radicals are held in close proximity, recombination will occur more frequently, thus reducing the rate of decomposition.

The pH (% neutralization) of the acrylic acid also had a surprising effect on the rate of decomposition of sodium persulfate. Decomposition occurs about three times faster at 0 and 25% neutralization than when neutralized 65% (Table V

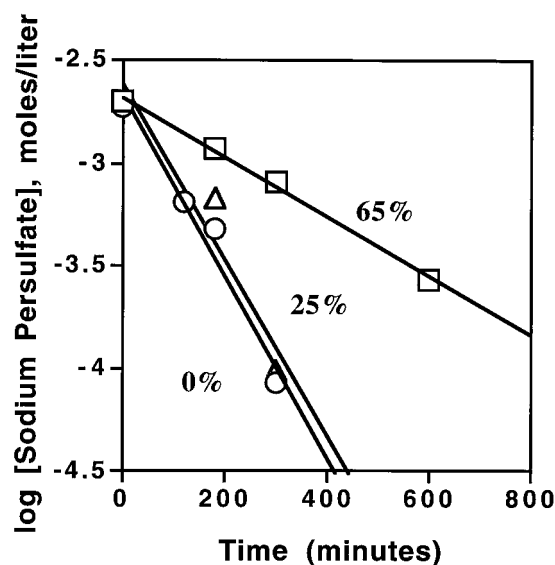


**Figure 5** Effect of % solids at 70°C on the rate of decomposition of sodium persulfate in 65% neutralized acrylic acid.

**Table V Rate of Decomposition of Sodium Persulfate vs. % Neutralization (pH) at 70°C**

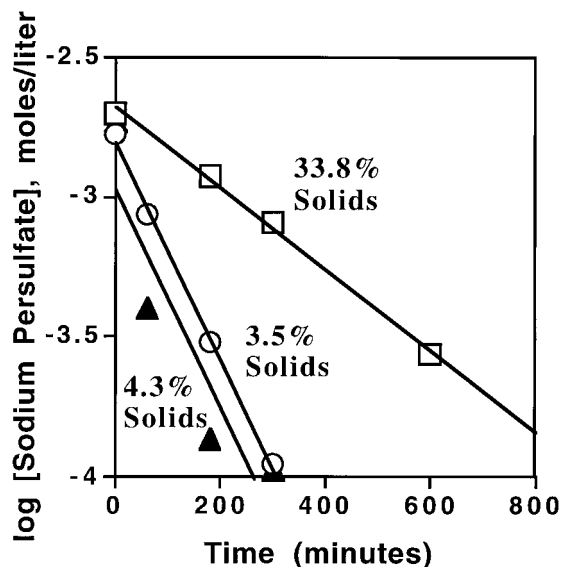
Neutralization (%)	Time (min)	Temp (°C)	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (ppm)	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (mol/L)
65	0	70	421	0.00198
65	180	70	230	0.00117
65	300	70	160	0.000815
65	600	70	53	0.000270
25	0	70	446	0.00198
25	180	70	140	0.000678
25	300	70	20	0.0000968
0	0	70	435	0.00185
0	120	70	138	0.000646
0	180	70	102	0.000478
0	300	70	18	0.0000843

and Fig. 6). The pH differences and range (2.6–4.7) are such that acid catalysis should not be an issue. The data are consistent with the charged electrolyte gel mechanism proposed previously to explain the % solids effects. At 25% neutralization, there are fewer sodium carboxylate groups than at 65% neutralization, at any given solids content. The low % neutralization reactions would have less ionic constraints on the mobility of charged species (e.g., sulfate ion radicals), and these systems were found to result in a faster rate of decomposition of the persulfate. Very highly



**Figure 6** Effect of % neutralization (pH) on the rate of decomposition of sodium persulfate at 70°C at a monomer concentration of 4.0M: 65% neutralized (pH 4.68), 25% neutralized (pH 3.94), and 0% neutralized (pH 2.62).





**Figure 7** Effect of % neutralization of acrylic acid and solids on the rate of decomposition of sodium persulfate at 70°C in the presence of monomers.

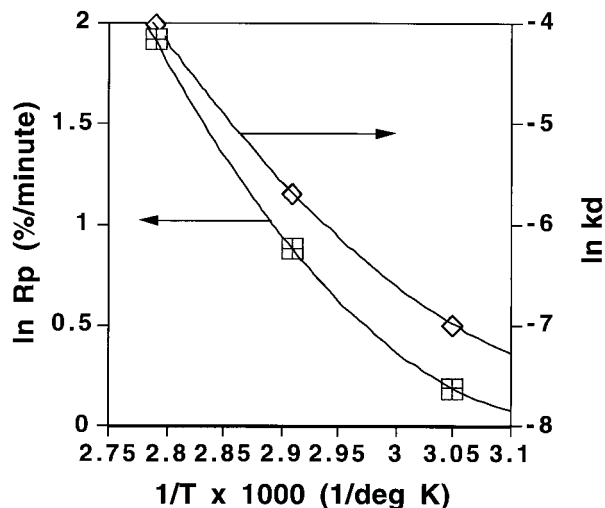
neutralized (125%) reaction mixtures at low solids (4.3%) had the same decomposition rate constant at 70°C as the 3.4% solids mixture at 65% neutralization (Fig. 7).

The rate constants for the decomposition of sodium persulfate in the presence of acrylic acid are tabulated in Table VI. The rate constants were calculated from the slopes of the data in Figures 5–7 multiplied by 2.3 to convert it to a natural log base.

The effect of temperature on the rate of decomposition of sodium persulfate also has an effect on the rate of polymerization. Although the activation energy for these processes is typically determined by the common  $1/T$  plot as shown pre-

**Table VI** Rate Constants for the Decomposition of Sodium Persulfate in the Presence of Acrylic Acid

Temperature (°C)	Neutralization (%)	Solids (%)	$k_d$ (mol/L/min)
70	0	33.8	$1.0 \times 10^{-2}$
70	25	33.8	$9.7 \times 10^{-3}$
70	65	33.8	$3.34 \times 10^{-3}$
70	65	3.4	$9.0 \times 10^{-3}$
70	125	4.3	$8.9 \times 10^{-3}$
70	65	16.9	$3.7 \times 10^{-3}$
55	65	33.8	$9.15 \times 10^{-4}$
85	65	33.8	$1.77 \times 10^{-2}$



**Figure 8** Relationship between the rate of decomposition of sodium persulfate in 65% neutralized acrylic acid solution and the initial rate of polymerization of 75% neutralized acrylic acid.

viously in Figure 4, with a linear relationship assumed, the persulfate decomposition in the presence of monomers appears to have some curvature in the plot. When the decomposition rate constant data, determined at 65% neutralization, are plotted on the same graph as polymerization rate data (determined by NMR on 75% neutralized samples),<sup>15</sup> a similar nonlinear relationship is seen (Fig. 8). This may be coincidental, but it is possible that the mechanism of persulfate decomposition is changing with temperature, or competitive mechanisms are operating. This is most evident at lower temperatures where induced decomposition effects would be more pronounced and where the rate differences from aqueous decomposition data are greatest (Fig. 4). This faster rate of decomposition of persulfate would be expected to result in a faster rate of polymerization, assuming resultant radical products.

## CONCLUSIONS

The rate of decomposition of sodium persulfate in the presence of acrylic acid was determined. Factors including the effect of percent neutralization (pH), temperature, and monomer concentration were studied. An analytical method to quantify sodium persulfate at levels as low as 10 ppm in the presence of acrylic acid was developed. Sodium persulfate decomposes faster in the pres-

ence of acrylic acid and partially neutralized acrylic acid than in buffered water. However, higher monomer concentrations of partially neutralized acrylic acid reduce the decomposition rate relative to low monomer concentrations. An ionic gel-cage mechanism is proposed to explain the results. The activation energy of sodium persulfate decomposition in 65% neutralized acrylic acid at 33.8% solids was determined to be 22.6 kcal/mol and the reaction was found to have a collisional frequency factor of  $8.6 \times 10^{11}$ .

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