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The dissociation rate coefficient of persulfate in emulsion polymerization systems

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Abstract

The effects of various components in an emulsion polymerization system on the dissociation rate coefficient of persulfate at 50 °C are examined using iodometry. Styrene monomer is found to enhance greatly the dissociation, while there is either no effect or possibly a slightly reduced rate of dissociation with methyl methacrylate monomer. The saturated analogues of these monomers (ethylbenzene and methyl isobutyrate) also enhance the dissociation, although not as much as styrene. Thus, such analogues should not be used as model compounds for determining the effect of a monomer on decomposition rate. The presence of metal parts in the reactor (e.g. as part of the agitation system) also could enhance the dissociation. The accelerations are consistent with literature mechanisms involving transfer reactions of aqueous-phase species. These results have significant implication for the interpretation and prediction of entry efficiencies and particle formation rates in emulsion polymerization systems.

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1. Introduction

The thermal dissociation of persulfate in water is very commonly used for radical generation in emulsion polymerization systems. Although the radical production process is commonly written as

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

it is well known that the actual reaction process is quite complex [1–4], involving steps in addition to that represented in Eq. (1). As with many reactions of polar species in the water phase, this process is sensitive to solvent effects (including changes in pH) and to the presence of metal ions, which can form a redox couple with persulfate (e.g. [5]) and thus catalyse the dissociation. Moreover, some of the reactions involved in the dissociation are particularly sensitive to the presence of polymerizable species (monomers) and indeed of many other aqueous-phase species (e.g. [6]). As an illustration of this, the rate of disappearance of persulfate is greatly increased in the presence of water-soluble alcohols (e.g. [7–9]) and of many vinyl monomers and even surfactants [6,8,10–25].

It is necessary to distinguish the kinetics of the disappearance of the parent persulfate anion (expressed in terms of the rate coefficient k_d in Eq. (1)) from those of prime interest in emulsion polymerization, viz., the appearance of growing radical species derived from monomer. This paper examines the former, and attempts to make reasonable conclusions regarding the latter.

Despite the extensive literature on this topic, there have been no systematic studies of the dissociation rate coefficient in a single system for a variety of different monomers and their saturated analogues. The reason for emphasizing that these studies be carried out in a single system is that even the presence of trace metal ions, such as from the impeller system or metal walls of a reactor, may have an effect, and so it is desirable to carry out a body of experiments in the one reactor rather than relying on comparison of results from different laboratories. The objective of this paper is to carry out such an investigation, in particular for systems containing styrene and methyl methacrylate (MMA), and their respective saturated equivalents, ethylbenzene and methyl isobutyrate. The systems used are chosen to mimic the conditions (e.g. with regard to

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temperature, and monomer and initiator concentrations) in emulsion polymerizations. We choose to study a surfactant-free system, so that effects of surfactants on k_d (as studied by Okubo and co-workers [24]) can be distinguished from those of the other components in a conventional emulsion polymerization.

The results from this study have a number of uses. First, the rate of initiator dissociation in a particular system yields information on the rate of initiator depletion: for example, if the dissociation is accelerated above that in a system with only pure water, then there could be unanticipated effects, e.g. unexpected initiator depletion, which obviously is undesirable. Second, models for particle formation (e.g. [26,27]) and for the rate coefficient for radical entry (initiator efficiency) into latex particles (e.g. [28]) always use the value of k_d, and clearly relating polymerization data to such mechanisms needs the true value of k_d. The aim of this paper is to obtain dissociation rate data for these purposes, and to consider these results in the light of some existing mechanistic theories. However, no attempt is made here to rigorously confirm or refute the range of mechanistic postulates that have been discussed by a number of authors [2,6,8,11,12,15,19–22].

A number of techniques have been used to investigate persulfate decomposition kinetics in aqueous media: iodometric and ferrometric titrations [9,10,17,25], redox titration based on cerium(III) oxidimetry [18], potentiometry and capillary electrophoresis [13], conductimetry [19–21], a gasometric method [6], anion exchange chromatography using reductive electrochemical detection [15], isotachophoresis [23,29], radiochemical methods [2,30] and a combination of rate measurements and electrospray mass spectrometry [22]. Many of these cannot be used in the presence of monomer in the water phase: for example, potentiometry relies on measurement of sulfate ions, but during polymerization some of these ions are present as end-groups on oligomers or polymer. The pH-based measurements are likely to be unreliable in monomer-containing systems, since the decomposition of persulfate is likely to be pH-sensitive (pH drops significantly in a pure persulfate experiment), and the means of measurement is based on an assumption that every decomposition event results in the addition of an initiator fragment to water, rather than to a monomer unit (which then invalidates the measurement).

The method chosen here for measuring k_d is based on the determination of persulfate by the ‘classic’ analytical iodometric titration technique of Kolthoff and Carr [17]. This approach is similar in principle to the method used by Bartlett and Cotman [9], except for the difference in titration procedure. The present procedure is applicable in the presence of species such as methyl methacrylate in water (which results in the formation of a latex), whereas many of the other techniques for measuring k_d cannot be used under these circumstances. Attempts were also made in the present paper to measure persulfate loss by Raman detection of a resonance associated with persulfate. However, this was found to be unsuitable, as detailed in Section 2.2.

2. Experimental

2.1. Iodometric method

Milli-Q water was used in all experiments. Potassium persulfate (KPS, BDH Analar grade) was recrystallized before use. The monomers, styrene (Huntsman, stabilized with 4-methoxyphenol inhibitor) and MMA (Mitsibushi Rayon, stabilized with 4-methoxyphenol inhibitor), were passed through a column of basic alumina and distilled under reduced pressure (first and last 10% discarded) to remove inhibitor before use.

Most experiments were carried out in a three-necked 1 L glass round-bottom flask, denoted ‘all-glass reactor’, fitted with a thermometer, a reflux condenser, and a rubber septum (the septum was isolated from the reaction mixture by a Teflon stop-cock). The flask was heated in an oil bath, with stirring provided by a magnetic stirring bar. The typical procedure was as follows. First, 470 mL of water was added to the reactor, and heated to the reaction temperature while sparging with a stream of argon for approximately 30 min. The appropriate amount of KPS required to give 500 mL of 10 mM persulfate solution was then dissolved in 30 mL of water and added to the reactor, and the reaction begun. Fifty millilitres samples of solution were removed at various times from the reaction vessel using a glass syringe and leur-lock needle, which had been purged with argon. The sample was immediately cooled in an ice bath. The concentration of undecomposed persulfate remaining was then determined using the iodometric procedure of Kolthoff and Carr [17]. Two 20 mL aliquots of the extracted sample were placed in separate conical flasks, to which 10 mL of a concentrated potassium iodide solution (4 g KI per 10 mL) was added. The flasks were left to stand for 15 and 30 min, respectively, (with occasional swirling), over which time the remaining persulfate present oxidized iodide to iodine, giving a yellow/brown colour. It was always found that 15 min standing time was adequate for complete evolution of iodine; however, it was useful to have duplicate results for all measurements. Finally, approximately 1 mL of glacial (∼17 M) acetic acid was added to the flask (to make the titration end-point clearer) and the amount of evolved iodine was determined by titration with standardized thiosulfate solution, using a starch indicator near the end-point. It was found that the colour change (from dark blue/black to colourless) associated with the end-point of this titration was distinct, and the end-point readily identified, even in the presence of latex particles. The pH of each untreated sample was also measured.

Some experiments were carried out in a 1-L computer-controlled reactor with a stainless steel impeller and base and top-plate. This will be referred to as the ‘mixed-materials reactor’. In these experiments, iodometric determination of undecomposed persulfate was carried out as above, except that at each sample time the 50 mL of reaction mixture was removed from the reactor (under positive nitrogen pressure) through a valve in the reactor’s base-plate.

The initial concentration of KPS, $[\mathrm{KPS}]_0$, was made to be 10 mM in all experiments. In each experiment, our iodometric procedure returned this starting value within error. For construction of first-order kinetic plots we always used the precise value of $[KPS]_0$ as prepared (as opposed to the less precise iodometric value).

A further experiment to test the possibility of any consumption of evolved iodine by organic additives was carried out as follows. Separate 20 mL aliquots of a standardized iodine solution were saturated with each organic additive and titrated with standardized thiosulfate solution in the usual manner. In all cases, no significant consumption of iodine was observed over the time scale of the titration (∼30 min).

As indicated above, duplicate samples were analyzed for each measurement, and all data points given in the figures below are duplicates. In most cases they cannot be distinguished on the scale of the figure, which evidences the excellent reproducibility of our iodometric procedure.

2.2. Measuring persulfate loss by Raman spectroscopy for MMA

An extensive attempt was made to obtain dissociation rate data using Raman spectroscopy. Raman spectra (excited at 514.5 nm) were obtained for high concentrations of KPS in water, and for water solutions of KPS containing MMA. Initial resonances corresponding to water (at ca. 3450 cm^{-1}) and persulfate (at ca. 1100 cm^{-1}) could be measured, although the persulfate resonances were weak. Useful results were obtained for the dissociation of persulfate in the water solution, which gave a value for k_d at 70 °C of $3.4\times10^{-5}\ \mathrm{s}^{-1}$ for a 60 mM solution (the literature value under these conditions [1] is $2.2\times10^{-5}\ \mathrm{s}^{-1}$).

For the MMA system, formation of insoluble MMA oligomers gave rise to phase separation in the reaction mixture, leading to cloudiness of the solution. This gave rise to scattering of the exciting radiation (and possibly also the scattered radiation). This rapidly decreased the signal levels of the detected Raman lines, such that the persulfate signals were undetectable after a short-time. Raman spectroscopy was therefore deemed unsuitable to measure persulfate dissociation kinetics in an MMA/water system.

Of course it would be preferable if modern spectroscopic methods could be used for probing matters such as persulfate decomposition in emulsion polymerization systems. However, our experiences above evidence the difficulty of employing such procedures, and they explain our reliance in this work on—and our recommendation of—a 'classic' but manifestly robust procedure for k_d determination.

3. Results and discussion

Fig. 1 shows data obtained at 50 °C in both the mixed-materials reactor and the all-glass reactor, with the initial concentration of persulfate being 10 mM and no other additives being present. The data are presented as plots of concentration as a function of time in the form appropriate for first-order kinetics (Eq. (1)), viz., $\ln([KPS]/[KPS]_0)$, where the subscript denotes the value at zero time. In both cases, it is seen that first-order rate behaviour is observed over an extended time period (up to 8 days). The evolution of pH is also shown; while the value of k_d depends on the pH, the data of Kolthoff and Miller at 50 °C [2] show that this effect is only ∼10% over the range of pH shown here.

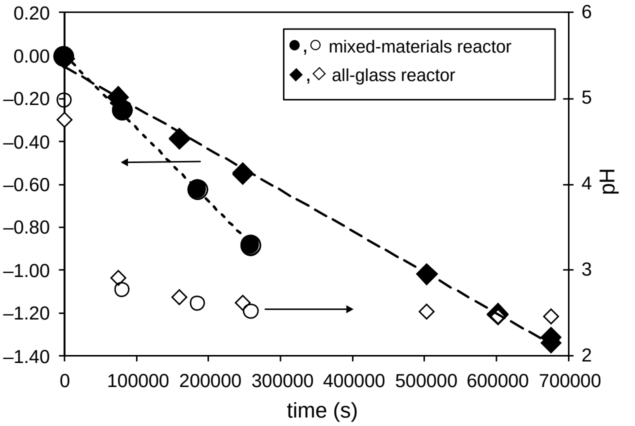

Fig. 1. Filled symbols: first-order plots of concentration (relative to concentration at zero time) as a function of time, for potassium persulfate at 50 °C, in an all-glass reactor and in a reactor constructed from mixed materials. Open symbols: pH dependence as a function of time.

While duplicate measurements from a given reactor showed excellent reproducibility, significantly different values were obtained for k_d for what should ostensibly be the same system but with different types of reactor, as shown in Table 1. The value at this temperature reported by Behrman and Edwards [1] is $1.1\times10^{-6}\ \mathrm{s}^{-1}$ (this is the value from their Arrhenius fit), compared with those found in the present study in the all-glass reactor ($1.9\times10^{-6}\ \mathrm{s}^{-1}$) and in the mixed-materials reactor ($3.4\times10^{-6}\ \mathrm{s}^{-1}$). The value in the all-glass reactor is in acceptable accord with both that of Behrman and Edwards and with other values reported in the literature at this temperature (e.g. [19]). The value in the mixed-materials reactor is

Table 1
Summary of rate data for persulfate dissociation measured by iodometry on a solution of 10 mM potassium persulfate (KPS) in water with various additives and under various conditions

Source/conditions	k_d ($10^{-6}\ \mathrm{s}^{-1}$)	For reactions in the all-glass reactor: ratio of k_d to that in the same system without organic additives
Behrman and Edwards [1]	1.1	–
KPS/water (all-glass reactor)	1.9[a]	1
KPS/water (mixed-materials reactor)	3.4[a]	–
KPS/water/EB	6.5[b]	3.4
KPS/water/MIB	2.3[b]	1.2
KPS/water/styrene run 1	4.7[c]	2.4
KPS/water/styrene run 2	3.3[c]	1.7
KPS/water/MMA	1.1[c]	0.6

[a] k_d obtained from fitting of data over all times.

[b] Initial k_d obtained from fitting of data over first three times (see text for explanation).

[c] Initial k_d obtained from initial slope of quadratic fit of data over all times (see text for explanation).

significantly higher. Given the operational differences between these two reactors (one being maintained at 50 °C by an oil bath and hot plate, the other by heated water flowing through a glass-walled jacket), it is reasonable to consider that a small difference in the operating temperature may account for some of the difference in measured k_d values. For example, one could expect a temperature difference between the two reactors of up to 2 °C, which, according to the Arrhenius fit of Behrman and Edwards [1], could explain a k_d difference of up to 40%. However, clearly this explanation cannot wholly account for the difference observed here, and it is postulated that this effect is due to trace amounts of metal ions deriving from metallic components in the mixed-materials reactor—it is well known that persulfate decomposition is catalysed by trace amounts of transition metal ions and other impurities. All subsequent runs in the present work used the all-glass reactor system, which is typical of that in many laboratory emulsion polymerizations. That said, it is recognized that the mixed-materials reactor more closely resembles industrial reactors.

The next set of data, given in Fig. 2 and Table 1, compares the persulfate dissociation rate in water with that when the water is saturated with ethylbenzene (EB, BDH Laboratory Reagent, used as received) and with methyl isobutyrate (MIB, synthesized by esterification of isobutyric acid (BDH) with methanol; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.14 (d, 6H), 2.52 (m, 1H), 3.64 (s, 3H)—in agreement with literature NMR data [31]), which are the saturated analogues of styrene and MMA, respectively. The experimental procedure was as above with 20 g of EB or MIB added at the start of the experiment, giving a 0.05 w/w emulsion in water. It is seen that addition of both MIB and EB significantly changes the kinetics. In each case, the reaction no longer obeys a simple first-order rate dependence, although the deviation is only noticeable over a period of time of more than a day, by which stage most emulsion polymerizations would be complete (i.e. this change in k_d with time most likely is not relevant for most emulsion polymerization modelling). It is reasonable to assume that this deviation from first-order kinetics is due to a build-up of species arising from side-reactions. Curiously, our results imply that with EB these species lower the value of k_d with time, while with MIB they raise it. In terms of the mechanisms discussed in Section 3.1 below, the MIB results make sense—there is buildup of species that may participate in transfer processes—but it is hard to understand this aspect of the EB results. One possibility is that EB acts directly as a transferring species TH, where H represents a labile hydrogen (as shown below, this is likely) and that its concentration diminishes with time as it is consumed. Given the high level of EB used (0.05 w/w in water), we consider the latter as unlikely.

Of greater importance is the observation that the first-order rate coefficient at early times is affected by the presence of EB and MIB. These values of k_d in Table 1 are from the slope of the plot over the first three times, i.e. up to 2 days. Although it is likely there is a slight change in k_d over even this time period, it seemed more statistically sensible to determine k_d from 3 points rather than just the minimum of two, and in this way to obtain an estimate of the 'initial' value of k_d. Our results are that k_d is not strongly affected but appears to be slightly increased by MIB, whereas EB causes a significant enhancement of the rate of disappearance of persulfate. An explanation for this will be given in Section 3.1. It is noted that these effects are too strong to be caused by changes in pH during the process: the evolution of the pH values, shown in Fig. 3, are over much the same range as those giving the good first-order plots in the absence of the organic additives.

The observation here that at 50 °C the presence of an emulsion of ethylbenzene causes an increase in k_d of a factor of $\sim$3 above that without EB agrees qualitatively with the conclusion of Santos et al. [13] of an increase with EB of a factor of 1.4 at 70 °C.

Last, we investigate persulfate decomposition in the presence of water/monomer emulsions, the monomers being styrene and MMA. In these cases, it is inevitable that a latex will form over time (by homogeneous nucleation [26]);

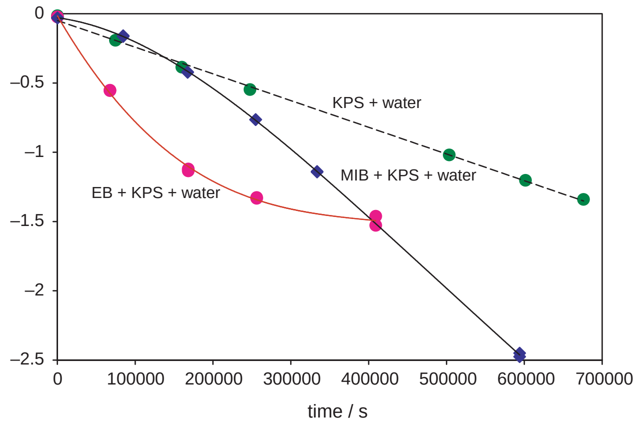

Fig. 2. First-order plots of concentration as a function of time for potassium persulfate (KPS) in water (data the same as in Fig. 1), and in the presence of emulsions of ethylbenzene (EB) and of methyl isobutyrate (MIB). All data are obtained in the all-glass reactor system.

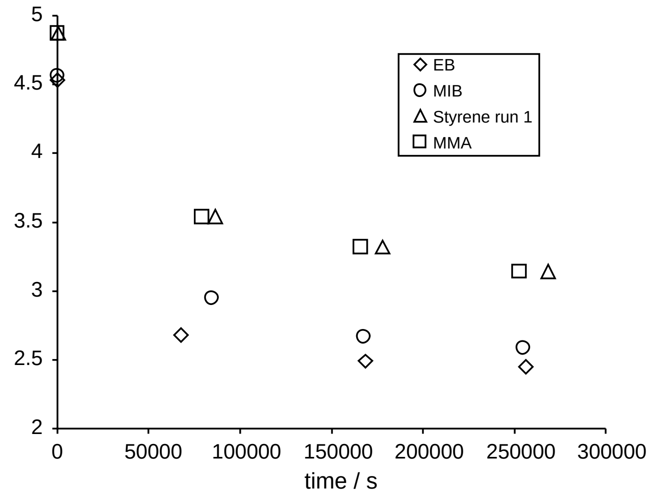

Fig. 3. Variation of pH over the course of the dissociation measurements for potassium persulfate (KPS); dissociation in the presence of emulsions of ethylbenzene (EB), methyl isobutyrate (MIB), styrene and methyl methacrylate (MMA).

moreover, any monomer will eventually be consumed through polymerization, and so it will gradually disappear from the aqueous phase. This is contrary to the aim of the present experiments, which was to measure the effect of monomer on k_d. Therefore, so as to ensure that persulfate decomposition always occurred in the presence of monomer in water, we adopted the approach of adding ∼10 g monomer at the start of the experiment, and then adding an additional 2.5 g of monomer just after each sample was extracted for analysis. Monomer was injected into the vessel through the rubber septum using a glass syringe and leur-lock needle in order to avoid addition of oxygen. While the presence of latex particles made the sample solutions opaque, it was still possible to clearly identify the end-point of the titration in the iodometric analysis.

Results are shown in Fig. 4. Two replicate runs with styrene emulsions are shown, to test reproducibility from experiment to experiment (as opposed to the duplicate sampling, which tested the reproducibility of the iodometric method; see Section 2.1). It is apparent that both monomers result in loss of simple first-order kinetics, but again only over long-time periods. However, it is evident that the effect is much weaker for MMA, as will be explained below. Values of k_d were obtained from the initial slope from a quadratic fit to the data (the values obtained from the 3-point method used for MIB and EB are the same within experimental uncertainty; the data for MMA were such that the k_d value from the quadratic fit was deemed more precise), and are given in Table 1. These refer to the initial rate of KPS decomposition, i.e. that which would be relevant to modelling of emulsion polymerization results.

It is seen that the presence of a styrene emulsion system significantly accelerates persulfate decomposition, whereas the MMA emulsion causes no such acceleration, and may in fact have a slight retardative effect on the decomposition. However, the latter is not a definite conclusion—it is possible that the MMA k_d is the same as that in pure water, within the margin of error of the present measurements. It is also evident that the effects of these monomers are not caused by the changes in pH, shown in Fig. 3, which again are in the same range as those for KPS without additives. Notably, these results are consistent with earlier observations by Brooks and Makanjuola [10] of persulfate decomposition at 60 °C. These authors also reported a significant enhancement in k_d for persulfate in the presence of a styrene emulsion system, and, while they did not observe a diminution in k_d in an MMA emulsion, they found no appreciable enhancement in that case, not inconsistent with our results. That said, Okubo and Mori [24] have questioned this finding, claiming that they observe the same decomposition kinetics in the presence of both MMA and styrene. However, their experiments also included surfactant, whereas the present ones are surfactant free—perhaps an important difference.

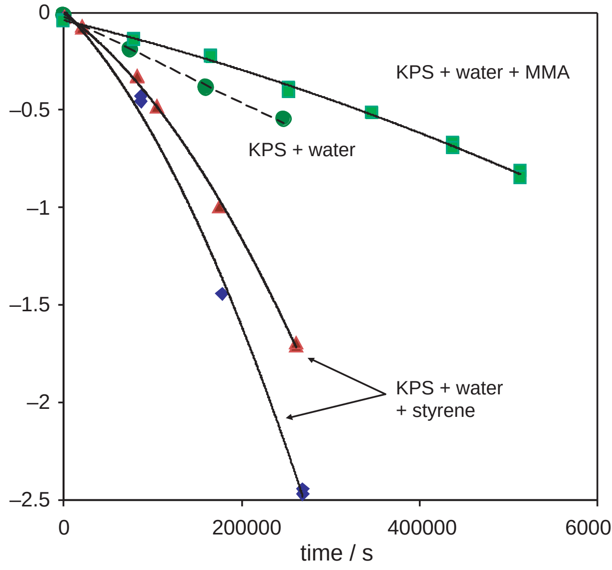

Fig. 4. First-order plots of concentration as a function of time for potassium persulfate (KPS) in water (data the same as in Fig. 1), and in the presence of emulsions of styrene (two replicate runs are shown) and of methyl methacrylate (MMA). All data are obtained in the all-glass reactor system.

3.1. Postulated mechanisms

The mechanism for persulfate dissociation at varying pH values and with the presence of various additives of varying concentrations has been an ongoing cause for debate in the literature for more than 50 years, and the present work does not aim to try to resolve the many outstanding questions. However, it is clearly of interest to see if mechanistic postulates of good standing (even if challenged by some authors) can be found, which are consistent with the present observations.

The acceleration observed with the addition of ethylbenzene and styrene is consistent with the transfer-catalysed mechanism first suggested by Crematy [25]

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

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^{-} + OH^{\cdot} \tag{3}$$

$$TH + OH^{\cdot} \rightarrow H_2O + T^{\cdot} \tag{4}$$

$$T^{\cdot} + S_2O_8^{2-} \rightarrow SO_4^{-\cdot} + SO_4^{2-} + \text{"reactive intermediate"} \tag{5}$$

$$T^{\cdot} + SO_4^{-\cdot} \rightarrow SO_4^{2-} + \text{"reactive intermediate and/or products"} \tag{6}$$

where TH is a species with significant transfer rate coefficient. Okubo and co-workers [23] suggest a similar transfer-catalysed mechanism except that $SO_4^{-\cdot}$ replaces $OH^{\cdot}$ in reaction (4) and mutual termination of $OH^{\cdot}$ is also included. Neither Crematy, Okubo nor the present authors specify the nature of the 'reactive intermediate(s)'; analyses of the aqueous phase in emulsion polymerizations (e.g. using isotachophoresis or electrospray [22,32]) reveal traces of many species, some of which are those predicted by direct reactions between persulfate and monomer, while others are yet to be specifically assigned.

The above reaction scheme can be compared to the 'reductive transfer' mechanism [20,22]:

$$^{-}SO_4M^{\cdot} \xrightarrow{M}\xrightarrow{M}\xrightarrow{M} {}^{-}SO_4M_i^{\cdot}$$

$$^{-}SO_4M_i^{\cdot} + S_2O_8^{2-} \rightarrow {}^{-}SO_4M_iSO_4^{-} + SO_4^{-\cdot} \qquad (7)$$

Here, M is an aqueous-phase monomer unit. In both reactions (5) and (7), induced decomposition consumes persulfate but generates no 'extra' radicals. In what follows, it is important to grasp that reaction (5) can potentially occur with any additive but reaction (7) is an additional pathway that can only occur in systems with monomer. Thus, the effect of EB and MIB on k_{d} is restricted to discussion of whether reaction (5) occurs while the effect of styrene and MMA must additionally include reaction (7).

EB is usually regarded as having relatively labile hydrogens and thus as being able to function as a transfer agent TH. Hence, it can accelerate persulfate decomposition by the above mechanism. On the other hand, styrene also accelerates the decomposition but is not a particularly strong transfer agent. However, after propagating with a sulfate radical in the aqueous phase and undergoing aqueous-phase termination by combination (which is the fate of most radicals generated from persulfate in a typical styrene emulsion system, which has low entry efficiency [28,33]), it forms species such as $^{-}OSO{-}CH_2{-}CH(Ph){-}CH(Ph){-}CH_2{-}OSO_3^{-}$ [32]. This and similar species arising from aqueous-phase termination are likely to have labile hydrogens (arising from the chemically similar structure causing the lability also likely to be responsible for the increase in k_{d} for persulfate in the presence of sodium dodecyl sulfate [23]). Hence, they can function as TH and participate in the transfer mechanisms given above to cause accelerated decomposition. Further, the aqueous-phase oligoradicals formed in styrene emulsion polymerization systems are relatively long-lived because of their slow propagation kinetics (due to the very low concentration of styrene in the aqueous phase), and it is possible that these oligoradicals directly induce decomposition, i.e. reaction (7). Given that the raise in k_{d} is observed right from the start, before there will have been any buildup of species such as $^{-}O_3SO{-}CH_2{-}CH(Ph){-}CH(Ph){-}CH_2{-}OSO_3^{-}$, it is perhaps to be considered most likely that it is the direct participation of oligoradicals that is primarily responsible for the elevated k_{d} at the beginning of styrene experiments. (It is noted that TH is unlikely to be styrene or MMA, because neither have labile hydrogens). Whatever, it is clear that there are physically reasonable explanations for the styrene and EB systems exhibiting an accelerated rate coefficient for dissociation of persulfate. Further, as (additional) TH species build up with time, one would expect k_{d} to increase further. This is consistent with our styrene results, but is at odds with our EB results, as already mentioned. The latter emphasizes the need for further investigation, for example, using spin-trapping techniques, in order to elucidate these matters, especially the nature of the postulated reactive intermediates and reactive products.

In summary, the initial enhancement of k_{d} in styrene is most likely caused by occurrence of reaction (7), while the further increase of k_{d} with time is most likely caused by increasing occurrence of reaction (5) as the concentration of aqueous-phase oligomers builds up with time. On the other hand, the initial enhancement of k_{d} in the presence of EB is most likely due to this additive functioning as TH and thereby leading to occurrence of reaction (5).

Next, we consider our MIB results, which show at most a weak increase (relative to the value in pure water) in k_{d} at early times, but a greater increase at longer times. At first, one would expect MIB to behave similarly to EB. However, Okubo and Mori [23] mention that $SO_4^{-\cdot}$ preferentially abstracts a hydrogen atom (to generate a $T^{\cdot}$ species) from the carbon adjacent to the terminal methyl group of an organic additive rather than from the terminal methyl group itself. Thus, one would expect a higher rate of induced decomposition in the presence of EB and only a weak enhancement in the presence of MIB, consistent with our results. However, that there almost certainly are processes like this still occurring in the presence of MIB is strongly suggested by the increase in k_{d} with time that is seen in these systems.

Now, we discuss our MMA results. The easy way to interpret these is that k_{d} is essentially the same as in pure water. Certainly, MMA has no readily labile hydrogen atoms (e.g. see the discussion of the paragraph above), so it is unlikely to have any capacity to function as TH. Further, it is predicted [28] to have a high entry efficiency, and so it should form relatively low concentrations of aqueous-phase termination products with labile hydrogens. Thus, the transfer-catalyzed acceleration postulated above (reaction (5)) will not be likely. Further still, aqueous-phase MMA oligoradicals will have relatively short aqueous-phase lifetimes (because propagation is fast due to the high aqueous-phase concentration of MMA), and so, in contrast to styrene, there will be little opportunity for these radicals to function as in reaction (7) before they undergo entry. For all these reasons one might expect the above chemistry to be largely absent in MMA systems, and thus for k_{d} to be as in pure water. As Okubo and Mori [23] have shown, the presence of monomer can effectively act as a radical trap for $SO_4^{-\cdot}$, thereby preventing induced decomposition from taking place. All this is more or less consistent with our MMA results, including that there is only a weak increase in k_{d} with time (see Fig. 4), most likely due (as with styrene) to accumulation of small but increasing amounts of aqueous-phase oligomers that give rise to occurrence of reaction (5). It is noted that, in contrast to our observation regarding the effect of methyl methacrylate on the rate of disappearance of persulfate, acrylates increase this rate [11,34], presumably for similar reasons to those given above regarding transfer-catalyzed dissociation in styrene systems.

More difficult to explain is the suggestion from our MMA results that this monomer might possibly reduce the rate coefficient for disappearance of persulfate. There is no obvious and established reason for this. One can postulate a relatively strong interaction between aqueous MMA and persulfate anions, which would change the polarity of the reactant and transition state and hence the dissociation rate coefficient, an effect seen for example in the propagation of acrylic acid [35]. Another possibility is to consider the following step, which causes loss of persulfate and has been proposed in addition to those given above [4]:

$$\mathrm{OH}^{\cdot} + \mathrm{S_2O_8^{2-}} \rightarrow \mathrm{HSO_4^-} + \mathrm{SO_4^{-\cdot}} + \frac{1}{2}\mathrm{O_2} \tag{8}$$

If aqueous MMA reacts very quickly with $\mathrm{OH}^{\cdot}$ to form a species, which cannot react directly with persulfate, then this would explain how addition of MMA could reduce the rate of persulfate loss. However, it is noted that arguments against the significance of reaction (8) have been put forward [1] (and indeed this cannot be a true elementary step because of the presence of $\frac{1}{2}O_2$). All that can be stated at this point is that there is no unchallengeable mechanistic explanation for a slight reduction in persulfate disappearance caused by the presence of MMA, and hence our results should only be taken as suggesting this as a possibility, not as establishing it. Of most importance for endeavours to understand the kinetics of emulsion polymerization is that MMA has essentially no effect on the rate of KPS dissociation.

Finally, it is instructive to revisit our pH results in the light of the above discussion. It is because of the generation of $\mathrm{HSO_4^-}$ that pH decreases with time as KPS decomposes. Reaction (3) is the principal fate of $\mathrm{SO_4^{-\cdot}}$ in pure water, and so a decrease of pH is observed in this system—see Fig. 1. As has been explained, the presence of additives provides alternative fates for $\mathrm{SO_4^{-\cdot}}$, ones which do not generate $\mathrm{HSO_4^-}$, and so it would be expected that pH is not decreased as much as in pure water. Comparison of the pH results of Figs. 1 and 3 confirms this general expectation. The effect is strongest for the styrene and MMA systems. Styrene we will discuss shortly, but the MMA results are easily explained: we believe this system involves little other radical chemistry than addition of radicals to MMA and then entry of these oligoradicals into latex particles. Thus, the formation of $\mathrm{HSO_4^-}$ from $\mathrm{SO_4^{-\cdot}}$ is minimized, and the decrease of pH is relatively small. On the other hand, in systems without latex particles, all $\mathrm{SO_4^{-\cdot}}$ radicals must find their fate in the aqueous phase. Where this is termination with $\mathrm{T}^{\cdot}$, there is no (direct) effect on pH. Where it is induced decomposition by reaction (5), there is regeneration of $\mathrm{SO_4^{-\cdot}}$, and thus there is every chance of the radical still ending up as $\mathrm{HSO_4^-}$. So the greater the extent to which induced decomposition occurs, the more pH should be reduced. Fully consistent with our k_d results, this is as observed for EB and MIB in the pH results of Fig. 3: both additives lower the pH compared with MMA, and for EB the effect is stronger, with pH in this system evolving almost exactly the same as for KPS in pure water (see Fig. 1).

Turning now to our styrene pH results, they show exactly the same trend as for MMA, i.e. minimal reduction. According to the logic above, this suggests minimal induced decomposition, which of course is at odds with our earlier conclusion that the elevated k_d of this system is due to extensive induced decomposition. This seeming contradiction is resolved by remembering that our earlier conclusion was in fact that k_d is enhanced in styrene systems primarily by the occurrence of reaction (7). Although this reaction regenerates $\mathrm{SO_4^{-\cdot}}$, this obviously will most likely just add to monomer and not end up as $\mathrm{HSO_4^-}$. In this way, it can be convincingly explained that pH evolution is the same in MMA and styrene but that k_d is significantly enhanced in styrene. Nevertheless, it is interesting that the pH results at first sight imply the same persulfate kinetics in both MMA and styrene, for this is what has been found by Okubo and Mori [24], who further found that k_d in styrene is the same as in pure water [23,29], contrary to our own findings and those of Brooks and Makanjuola [10]. Possibly, this discrepancy is related to the employment of different methods to measure persulfate concentration (isotacophoresis by Okubo and Mori, versus iodometric and ferrometric titrations here and by Brooks and Makanjuola), or possibly it is related to Okubo and Mori generally having surfactant also present (although if anything this should only raise k_d). This inconsistency is curious.

Our results should not be over-analyzed with regard to mechanism. The main purpose of the present analysis was to obtain data for the effect of emulsion polymerization systems on persulfate decomposition, not to undertake a mechanistic investigation.

3.2. *Inferences for emulsion polymerization mechanisms*

The results from this study have major implications for the interpretation of rate data from emulsion polymerizations, in particular those for free-radical entry into latex particles.

A model for this entry event, the so-called 'Maxwell–Morrison' model [28], has proved able to rationalize a large amount of data for electrostatically stabilized latex particles [28,36–42], and has withstood a range of experimental tests, such as predicted dependences on particle size [36] and the charge on both the particle and the entering radical [38], tests which could have refuted its assumptions. The essence of this model is its assumption that initiator-derived radicals propagate and terminate in the aqueous phase, and enter a particle if and only if they achieve a critical degree of polymerization z; all z-mers enter and have no other fate if particles are present. The rate equations quantifying this are given by:

$$\text{initial propagation step: } \mathrm{I}^{\cdot} + \mathrm{M} \xrightarrow{k_{\mathrm{pI}}} \mathrm{IM}^{\cdot} \tag{9}$$

$$\text{subsequent aqueous-phase propagation: } \mathrm{IM}_i^{\cdot} + \mathrm{M} \xrightarrow{k_{\mathrm{p,w}}^{i}} \mathrm{IM}_{i+1}^{\cdot} \tag{10}$$

$$\text{aqueous-phase termination: } \mathrm{IM}_i^{\cdot} + \mathrm{T}^{\cdot} \xrightarrow{k_{\mathrm{t,w}}} \text{inert products}, \ i < z \tag{11}$$

$$\text{entry: } \mathrm{IM}_z^{\cdot} + \text{latex particle} \xrightarrow{\rho} \text{entry} \tag{12}$$

Here, $\mathrm{I}^{\cdot}$ is an initiator radical ($\mathrm{SO_4^{-\cdot}}$ in the present case), ρ is the first-order entry rate coefficient (the frequency with which radicals enter particles), and where, for simplicity, the dependence of the termination rate coefficient on the degree of polymerization of the two terminating radicals (chain-length-dependent termination [43,44]) has been ignored. If various reasonable assumptions are made, including that reaction (9) is so fast as not to be rate-determining and that all are the same, then one obtains a simple analytic expression for ρ

$$\rho \approx \frac{2k_{\mathrm{d}}[\mathrm{I}]N_{\mathrm{A}}}{N_{\mathrm{p}}}\left\{\frac{\sqrt{2k_{\mathrm{d}}[\mathrm{I}]k_{\mathrm{t,w}}}}{k_{\mathrm{p,w}}[M]_{\mathrm{w}}}+1\right\}^{1-z} \qquad (13)$$

where [I] is the initiator concentration, N_{A} the Avogadro constant, N_{p} the number of latex particles per unit volume of the aqueous phase, and $[\mathrm{M}]_{\mathrm{w}}$ the aqueous-phase monomer concentration.

Most of the applications of the model have been to styrene. While the first applications of this model allowed k_{d} to vary [28], subsequent applications have assumed the value given by Behrman and Edwards [1]. If it is assumed that all $k^{i}_{\mathrm{p,w}}$ are the same and are the well-established result for styrene in solution and in bulk [45,46], the data for ρ for entry of persulfate-derived radicals into latexes stabilized with ionic surfactants are fitted by $z=2$, a value, which can be rationalized [28] in terms of the degree of polymerization required to make a surface active z-mer.

Clearly, the result that styrene increases the rate of dissociation of persulfate has significant implications for data interpretation. It is essential to be aware that the present experiments measure the rate of disappearance of persulfate, not the rate of formation of $^{\cdot}\mathrm{MSO}_4^-$, species which the model takes to be formed very quickly each time a dissociation event takes place. Given the plethora of possible reactions of persulfate given above, it may well be that the rate of this step is not simply $2k_{\mathrm{d}}[\mathrm{I}]$, the value we have always assumed to date—reasonably, given the lack of any further information—in our modelling work (e.g. [28,38]). The usual approach for accommodating this possibility is to replace k_{d} with the quantity fk_{d}, where f is the so-called 'initiator efficiency', taking a value less than or equal to unity and assumed to be independent of initiator concentration. In the absence of a more complete understanding of the mechanism for persulfate decomposition, this simple treatment may be the best approach. However, it is noted that, in practice, the values of f and k_{d} may only be separated by combining results from experiments of the present sort (giving the value of k_{d}) with those from experiments measuring the actual yield of polymerizing radicals (the value of fk_{d}), for example radical trapping experiments.

To explore the effect on emulsion polymerization kinetics of the findings of the present work, data on the entry rate coefficient for styrene [38] with persulfate were refitted with the increased value of k_{d} given in Table 1, viz., the mean value from the two runs of $4\times10^{-6}\ \mathrm{s}^{-1}$. The values of z (which was restrained to be an integer), $k_{\mathrm{t,w}}$, and $k^{i}_{\mathrm{p,w}}$ were allowed to vary in a non-linear least-squares fit. The results of this fit, and the original one with the Behrman/Edwards value of k_{d}, are given in Fig. 5 and Table 2. It is of note that the data could not be adequately fitted with an integer value of z greater than 2 while having physically reasonable values of $k^{i}_{\mathrm{p,w}}$ and $k_{\mathrm{t,w}}$.

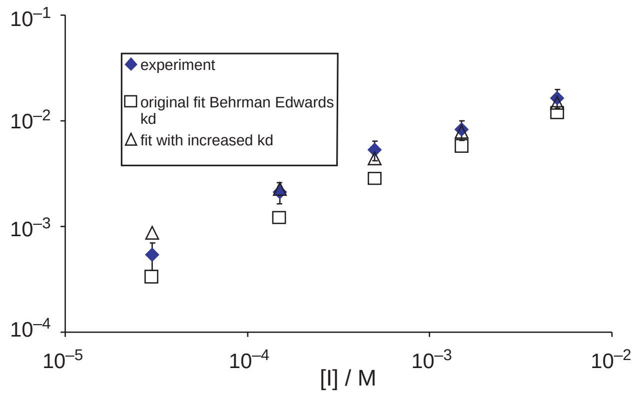

Fig. 5. Data for the entry rate coefficient in a styrene/persulfate seeded emulsion polymerization [38] fitted to the model of Maxwell et al. [28] assuming the value of k_{d} reported by Behrman and Edwards [1], and that found in the present study for a styrene emulsion system. Fitting parameters given in Table 2.

It is seen that refitting the data with the significantly larger value of k_{d} (measured in the present work under styrene emulsion conditions) was still possible using physically reasonable values of the aqueous-phase termination and propagation rate coefficients, and with the same value of z as in the fit using the smaller k_{d} value of Behrman and Edwards (obtained from dissociation studies in the absence of a styrene emulsion).

Two points are to be borne in mind when considering the impact of the present results on emulsion polymerization kinetics: (1) We reiterate the important point made earlier that most emulsion polymerizations are over relatively quickly (1 day or less) on the timescale of the present measurements of persulfate concentration (several days). Thus, our finding of k_{d} varying over the timescale of days is of itself unlikely to be of relevance to modelling of kinetics. Where there could be an indirect relevance is if an emulsion polymerization has such a marked buildup of transfer-capable species that k_{d} changes significantly within one day. (2) In this work, k_{d} has been defined, as usual, as describing the net rate of disappearance of persulfate. Once additional reactions for persulfate disappearance—most notably induced decomposition—become significant, k_{d} is no longer the rate coefficient for the elementary reaction of persulfate dissociation. Because induced decomposition gives no net change to overall radical concentration, one therefore cannot necessarily regard k_{d} as representing the rate of generation of polymerization-starting radicals, i.e. k_{d} is not

Table 2
Parameters used to fit entry rate coefficient data

Quantity	Fit using k_{d} of reference [1]	Fit using k_{d} for styrene-containing system measured in this work ($4\times10^{-6}\ \mathrm{s}^{-1}$)
$k_{\mathrm{d}}/\mathrm{s}^{-1}$	1.1×10^{-6}	4×10^{-6}
z	2	2
$k^{1}_{\mathrm{p,w}}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	236	358
$k^{2}_{\mathrm{p,w}}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	236	236
$k_{\mathrm{t,w}}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	1.75×10^{9}	2.36×10^{10}

necessarily the quantity to be used in seeking to understand emulsion polymerization kinetics, whether those of particle formation or of particle growth. In this context, it is clear that the two issues raised here warrant further investigation.

4. Conclusions

Using iodometric titration, it was found that the dissociation rate of persulfate in water at 50 °C in conditions consistent with conventional emulsion polymerizations was significantly increased by the presence of ethylbenzene and styrene, while it is much the same or possibly slightly decreased by the presence of methyl methacrylate. The systems with organic additives also showed deviation from first-order kinetics at very long times. The increased values can be rationalized in terms of a transfer-catalyzed mechanism; there is no obvious explanation for an apparent decrease of rate with MMA. Importantly, we found that saturated monomer analogues should not be used as model compounds for determining the effect of a monomer on k_d: even if EB were not too different to styrene in its effect on k_d, and likewise for MIB/MMA, it is clear from the present work that there is no substitute for measuring k_d under actual emulsion polymerization conditions. The titrimetric approach employed here is technically undemanding and, although a 'classical' technique, is able to yield the requisite data in a system, which is close to that of an actual emulsion polymerization. It was also observed that performing the same measurements in a reactor made of mixed materials, including stainless steel, also led to an increased dissociation rate coefficient, although first-order loss kinetics were still obeyed; this effect may be ascribed to trace amounts of impurities such as metal ions.

The large changes in dissociation rate coefficient in the presence of aqueous-phase monomer have implications for the interpretation of data for radical entry in emulsion polymerizations. Refitting data for a styrene/persulfate emulsion system using the 'Maxwell–Morrison' entry model [28] (which assumes entry occurs only as a result of aqueous-phase propagation of monomer to a critical degree of polymerization z) with a fourfold increase of dissociation rate coefficient results in only quantitative but not qualitative changes to the inferences of the model.

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