# Iron-Accelerated Cumene Hydroperoxide Decomposition in Hexadecane and Trilaurin Emulsions

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Free radicals arising from lipid peroxides accelerate the oxidative deterioration of foods. To elucidate how lipid peroxides impact oxidative reactions in food emulsions, the stability of cumene hydroperoxide was studied in hexadecane or trilaurin emulsions stabilized by anionic (sodium dodecyl sulfate; SDS), nonionic (Tween 20), and cationic (dodecyltrimethylammonium bromide; DTAB) surfactants. $Fe^{2+}$ rapidly (within 10 min) decomposed between 10 and 31% of the cumene hydroperoxide in Tween 20- and DTAB-stabilized emulsions at pH 3.0 and 7.0 and in the SDS-stabilized emulsion at pH 7.0 with no further decomposition of peroxides occurring for up to 3 h. In SDS-stabilized emulsions at pH 3.0, $Fe^{2+}$ decreased peroxides by 90% after 3 h. Decomposition of peroxides in the absence of added iron and by $Fe^{3+}$ was observed only in SDS-stabilized emulsions at pH 3.0. These results suggest that peroxide decomposition by iron redox cycling occurs when iron emulsion droplet interactions are high.

**Keywords:** *Lipid oxidation; emulsions; iron; rancidity; surfactants*

## INTRODUCTION

Lipid oxidation is a free radical chain reaction with important consequences for living systems and food quality. Lipid oxidation in foods can result in rancidity, and in biological systems it can result in cell damage and increased risk for cancer and cardiovascular disease (Kubow, 1993). Lipid peroxides are a common component of commercially available unsaturated lipids (Halliwell et al., 1995). Lipid peroxides are relatively stable unless subjected to high temperatures, transition metals, or UV light, which will accelerate their breakdown into free radicals that further promote lipid oxidation (Nawar, 1996). In many processed foods, lipids are dispersed as small droplets in an aqueous continuous phase. In these systems nonpolar lipids partition into the droplet interior, whereas the more polar lipid peroxides tend to align at the lipid−water interface (Buettner, 1993; Coupland and McClements, 1996). Localization of lipid peroxides at the interfacial region may increase their reactivity due to their ability to interact more readily with aqueous phase prooxidants (e.g., transition metals).

One of the major mechanisms by which iron, the most ubiquitous transition metal found in foods, promotes lipid oxidation is by catalyzing the breakdown of peroxides into free radicals. This prooxidant activity of iron depends on factors such as its chemical state, solubility, and physical location. The ferrous state of iron ($Fe^{2+}$) is capable of decomposing peroxides $>10^7$ times more rapidly than ferric ions ($Fe^{3+}$) at 25 °C and pH 7.0 (Dunford, 1987). Ferrous and ferric ions react with lipid peroxides to form alkoxy and peroxy radicals, respectively (Frankel, 1991):

$$LOOH + Fe^{2+} \rightarrow LO^{\bullet} + Fe^{3+} + OH^{-}$$

or

$$LOOH + Fe^{3+} \rightarrow LOO^{\bullet} + Fe^{2+} + H^{+}$$

Alkoxy ($LO^{\bullet}$) and peroxy ($LOO^{\bullet}$) radicals are both capable of abstracting hydrogen from unsaturated fatty acids and thereby further promoting lipid oxidation, with alkoxy radicals being more reactive than peroxy radicals (Buettner, 1993). $Fe^{2+}$ is in part more reactive than $Fe^{3+}$ due to differences in water solubility, with $Fe^{2+}$ being $10^{13}$ and $10^{17}$ times more water soluble than $Fe^{3+}$ at pH 3 and 7, respectively (Zumdahl, 1983). However, $Fe^{3+}$ is more common in foods (Clydesdale, 1988), suggesting that, despite its low reactivity and solubility, it may be an important prooxidant that impacts the long-term oxidative stability of foods (Halliwell and Guterridge, 1984).

The ability of iron to promote lipid oxidation in emulsions can be affected by iron's ability to interact with lipids at the emulsion droplet interface. Using 5% corn oil-in-water emulsions stabilized by anionic (sodium dodecyl sulfate; SDS), nonionic (polyoxyethylene 10 lauryl ether; Brij), and cationic (dodecyltrimethylammonium bromide; DTAB) surfactants (0.017 M), Mei et al. (1998a) found that iron-promoted lipid oxidation rates were highest in SDS-stabilized emulsion droplets and lowest for Brij- and DTAB-stabilized emulsions. At lower pH values (3−5), lipid oxidation increased for SDS-stabilized emulsions but did not change for Brij- and DTAB-stabilized emulsions. Zeta potential measurements have shown that both $Fe^{2+}$ and $Fe^{3+}$ can associate with SDS-stabilized emulsion droplets, but not with nonionic Brij-stabilized and cationic DTAB-stabi-

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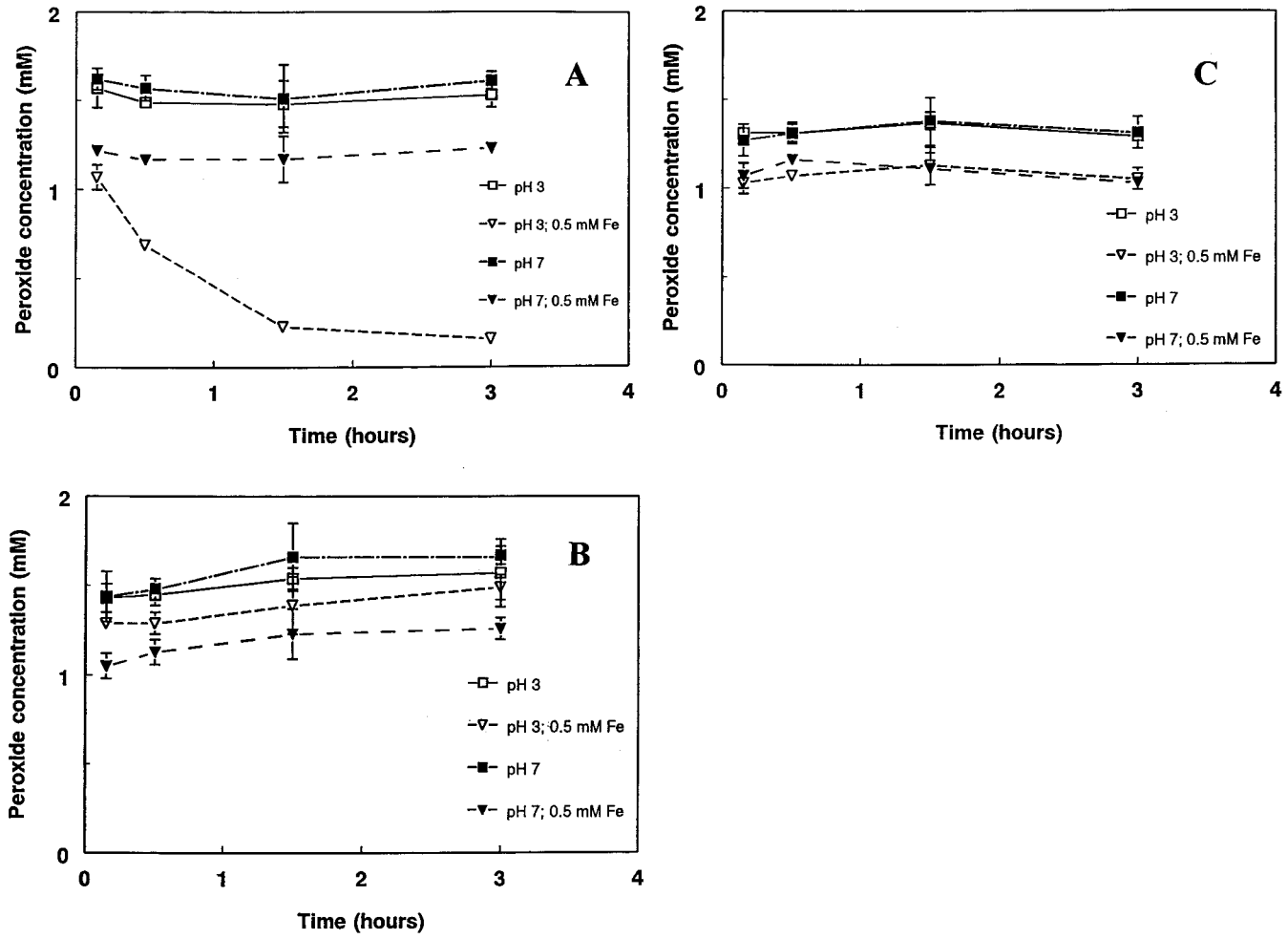


**Figure 1.** Effect of 0.5 mM $Fe^{2+}$ on the decomposition of cumene hydroperoxide in (A) SDS-, (B) Tween 20-, and (C) DTAB-stabilized hexadecane emulsions at pH 3.0 or 7.0. Emulsions were incubated at 55 °C.

lized emulsion droplets (Mei et al., 1998b). In addition, factors that decreased iron interactions with SDS-stabilized emulsion droplets such as increasing pH, chelators (e.g., EDTA and phytate), and NaCl resulted in decreased lipid oxidation rates (Mei et al., 1998a,b). The charge of protein-stabilized emulsions also influences the ability of iron to promote lipid oxidation. In emulsified menhaden oil (5%) stabilized by whey protein isolate (p$I \cong 5.1$), lipid oxidation rates were lowest at pH 3.0 (positively charged emulsion droplets) and highest at pH 7.0 (negatively charged emulsion droplets), whereas the opposite was observed in nonionic Tween 20-stabilized emulsions (Donnelly et al., 1998). The ability of surfactant charge to influence peroxide-dependent lipid oxidation has also been observed in lipid micelles (Fukuzawa and Fujii, 1992; Yoshida and Niki, 1992).

Because the ability of iron to promote lipid oxidation is influenced by its ability to decompose lipid peroxides, the objective of this study was to gain a better understanding of some of the factors impacting iron−lipid peroxide interactions in oil-in-water emulsions. This was accomplished using a model system consisting of SDS-, Tween 20-, or DTAB-stabilized hexadecane or trilaurin emulsions containing cumene hydroperoxide. $Fe^{2+}$ and $Fe^{3+}$ were used to promote hydroperoxide decomposition. Hexadecane and trilaurin were used as two different nonoxidizing lipid sources so that additional peroxides would not be created from free radicals originating from peroxide decomposition. Understanding the factors governing the interaction of iron with peroxides in emulsion droplets could provide insights on how to develop new techniques to control lipid oxidation in food emulsions.

## MATERIALS AND METHODS

**Materials.** Hexadecane, trilaurin, cumene hydroperoxide, polyoxyethylene sorbitan monolaurate (Tween 20), dodecyltrimethylammonium bromide (DTAB), and 2,2′-dipyridyl were purchased from Sigma Chemical Co. (St. Louis, MO). Sodium dodecyl sulfate (SDS) was obtained from Aldrich Chemical Co. (Milwaukee, WI). Disodium ethylenediaminetetraacetic acid (EDTA) and sodium chloride were purchased from Curtin Matheson Scientific, Inc. (Houston, TX). All other reagents were of analytical grade or purer.

**Preparation of Emulsions.** Emulsions were prepared by mixing either hexadecane or trilaurin containing ∼22 mM cumene peroxide with aqueous solutions of SDS, Tween 20, or DTAB (0.017 M) in an acetate−imidizole buffer solution (5 mM each) to give a final emulsion of 5% lipid. The buffer solution was previously tested and found not to interfere with the ability of iron to promote oxidation in oil-in-water emulsions (Mei et al., 1998a). Elevated temperatures (50 °C) were used during emulsion preparation to maintain trilaurin in a liquid state. Solutions were sonicated for 3−6 min using a Braun-Sonic 2000 U ultrasonic generator (Braun Biotech, Allentown, PA) equipped with a 5T standard probe at a power setting of +200 and a 0.3 s repeating cycle (Mei et al., 1998a) to obtain mean emulsion droplet diameters of 0.19−0.23 $\mu$m. Particle size distributions were measured using a Horiba LA-900 laser scattering particle size distribution analyzer (Horiba

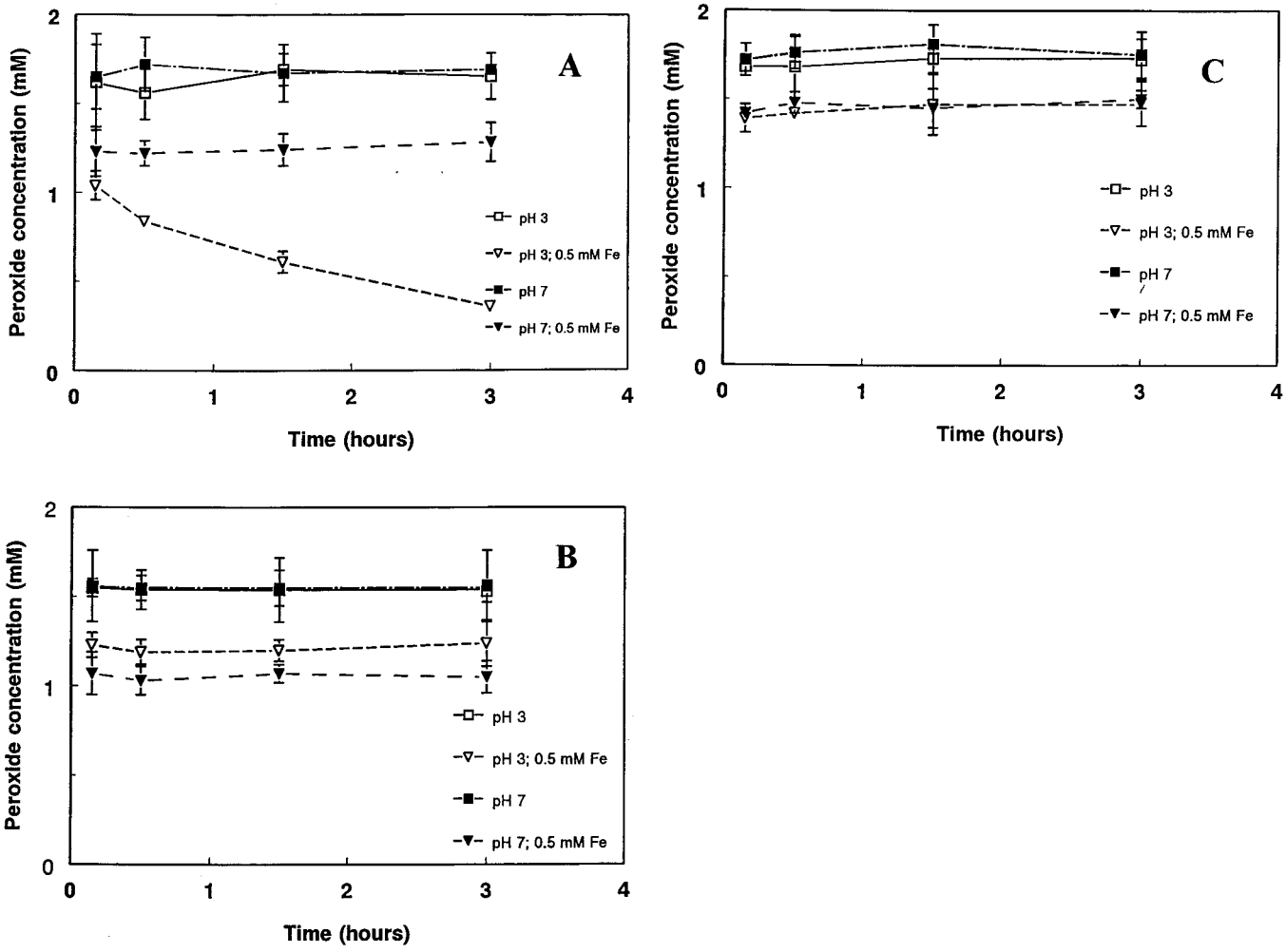


**Figure 2.** Effect of 0.5 mM $Fe^{2+}$ on the decomposition of cumene hydroperoxide in (A) SDS-, (B) Tween 20-, and (C) DTAB-stabilized trilaurin emulsions at pH 3.0 or 7.0. Emulsions were incubated at 55 °C.

Instruments, Irvine, CA) (Weiss et al., 1996). Particle size distributions were measured periodically and did not change over the course of the experiments. The sonication conditions used did not alter initial peroxide concentrations. EDTA (0.05−2.0 mM) and NaCl (3.0−170.0 mM) were added to the emulsions prior to the addition of iron. All experiments were started within 20 min after emulsion preparation.

**Determination of Peroxide Concentrations.** Peroxide decomposition was promoted by either ferrous sulfate or ferric chloride in emulsions incubated at 55 °C, with the exception of one long-term hexadecane emulsion study that was conducted at 20 °C. Peroxides were extracted at various time intervals by adding 0.3 mL of emulsion to 1.5 mL of isooctane/isopropanal (3:2 v/v), followed by vortexing three times for 10 s each. After centrifugation for 2 min at 2000*g*, 0.2 mL of the clear upper layer was collected, and peroxides were quantitated using a modified method of Shanta and Decker (1994). The sample extract (0.2 mL) was mixed with 2.8 mL of methanol/1-butanol (2:1 v/v) and 30 $\mu$L of thiocyanate/$Fe^{2+}$ solution and then vortexed. The thiocyanate/$Fe^{2+}$ solution was made by mixing one part 3.94 M thiocyanate solution with one part 0.072 M $Fe^{2+}$ solution (obtained from the supernatant of a mixture of one part 0.144 M $FeSO_4$ and one part 0.132 M $BaCl_2$ in 0.4 M HCl). After 20 min of incubation at room temperature, absorbance was measured at 510 nm. Peroxide concentrations were determined using a cumene hydroperoxide standard curve.

**Measurement of $Fe^{2+}$ Concentrations.** $Fe^{2+}$ was quantified colorimetrically using a method adapted from Fukuzawa and Fujii (1992). Two hundred microliters of emulsion was dissolved into 2.8 mL of methanol/butanol (2:1 v/v) containing 2,2′-dypyridyl (final concentration = 5 mM), and the absorbance was measured at 520 nm after 2 min. $Fe^{2+}$ concentration was determined using a standard curve prepared using ferrous sulfate.

**Statistical Analysis.** Assays were preformed on triplicate samples. Statistical analysis was performed using the Student *t*-test (Snedecor and Cochran, 1989).

## RESULTS

**$Fe^{2+}$-Promoted Cumene Hydroperoxide Decomposition As Affected by Surfactant Charge and pH.** Cumene hydroperoxide in hexadecane emulsions made with anionic (SDS), nonionic (Tween 20), and cationic (DTAB) surfactants showed different rates of $Fe^{2+}$ (0.5 mM)-promoted decomposition (Figure 1). To compare the effect of $Fe^{2+}$ on cumene hydroperoxide decomposition, the same emulsions (within a surfactant type), with and without added iron, were incubated for 3 h. In all of the emulsions without added $Fe^{2+}$, peroxides were stable at both pH 3.0 and 7.0 for the entire 3 h incubation period. Addition of $Fe^{2+}$ (0.5 mM) caused a decrease in cumene hydroperoxide concentrations in emulsions stabilized by SDS, Tween 20, and DTAB ($p \leq 0.05$). In the SDS-stabilized hexadecane emulsion at pH 3, $Fe^{2+}$ (0.5 mM) caused a 32% decrease in peroxide concentrations during the first 10 min compared to the emulsion without iron (control), followed by a more gradual decline, resulting in a 90% loss of peroxides at 3 h (Figure 1A). At pH 3, $Fe^{2+}$ (0.5 mM) decreased peroxides 21 and 10%, in the DTAB- and

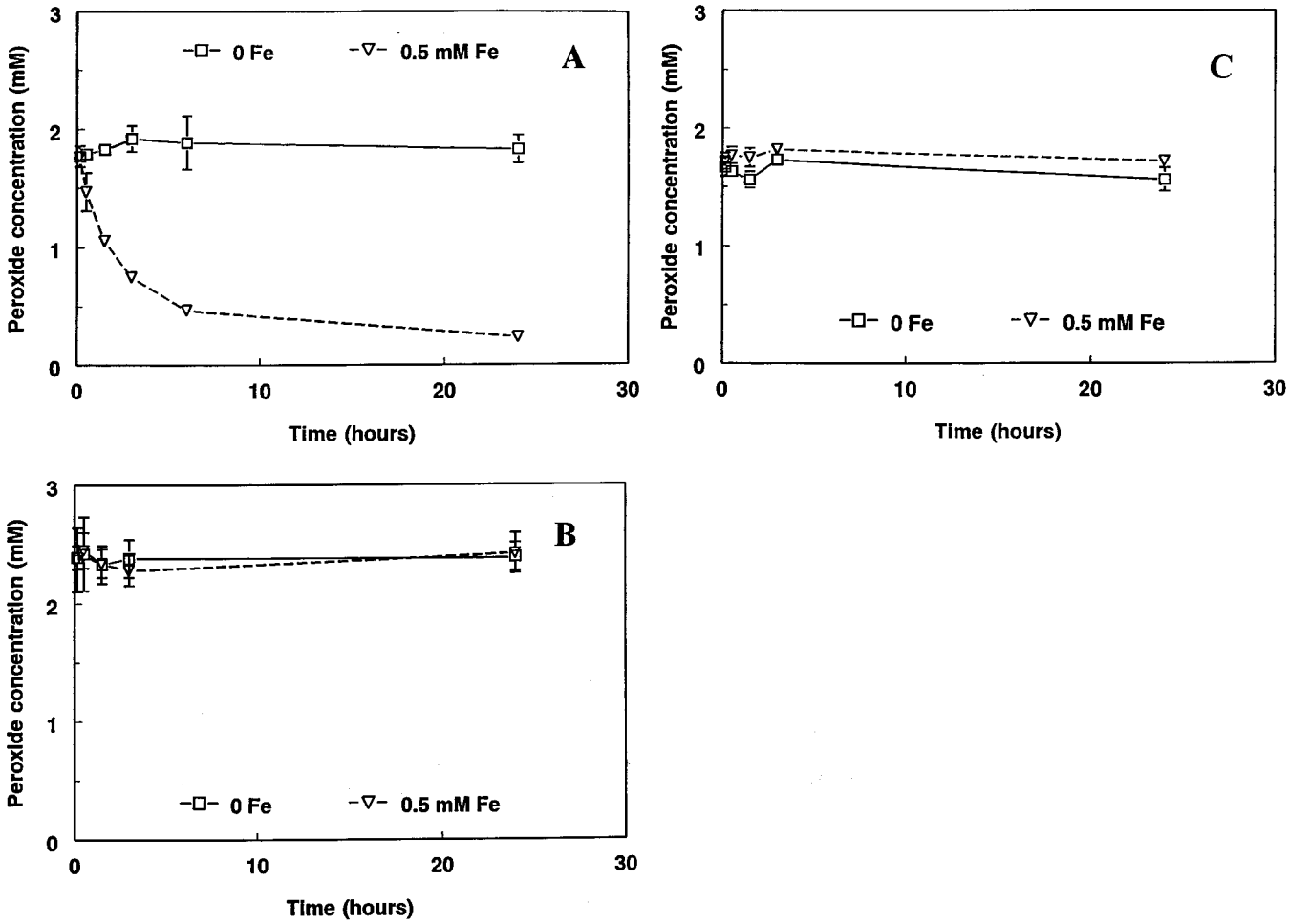


**Figure 3.** Effect of 0.5 mM $Fe^{3+}$ on the decomposition of cumene hydroperoxide in (A) SDS-, (B) Tween 20-, and (C) DTAB-stabilized trilaurin emulsions at pH 3.0. Emulsions were incubated at 55 °C.

Tween 20-stabilized hexadecane emulsions, respectively, during the first 10 min of incubation, compared to the controls, with no further peroxide decomposition occurring for up to 3 h (Figure 1B,C). At pH 7.0, $Fe^{2+}$ (0.5 mM) decreased peroxides 25, 27, and 16% for SDS-, Tween 20-, and DTAB-stabilized hexadecane emulsions, respectively, during the first 10 min of incubation (compared to the control), after which time peroxide concentrations remained constant (Figure 1).

Emulsions made with trilaurin exhibited $Fe^{2+}$-promoted cumene hydroperoxide decomposition patterns similar to those of the hexadecane emulsions (Figure 2). At pH 3 and 7, $Fe^{2+}$ (0.5 mM) decreased cumene hydroperoxide concentrations during the first 10 min of incubation in the SDS-stabilized trilaurin emulsion 36 and 25%, respectively, compared to emulsions without iron (Figure 2A). In the SDS-stabilized trilaurin emulsions, decomposition of peroxides was observed for up to 3 h at pH 3, whereas at pH 7.0 peroxide concentrations remained constant after the initial reduction. During the first 10 min, $Fe^{2+}$ (0.5 mM) decreased peroxides 17% (pH 3) and 18% (pH 7.0) in the DTAB-stabilized trilaurin emulsions (Figure 2B) with no further decomposition of peroxides being observed for up to 3 h. The initial decomposition (10 min) of peroxides in the Tween 20-stabilized trilaurin emulsions was 21% at pH 3 and 31% at pH 7.0, after which there was no further loss of peroxides for up to 3 h (Figure 2C). $Fe^{2+}$-promoted decomposition of peroxides in the Tween 20-stabilized emulsions was greater at pH 7.0 than at pH 3.0 for both the hexadecane ($p \leq 0.05$; Figure 1B) and trilaurin ($p \leq 0.10$; Figure 2B) emulsions. These results are similar to research that has shown that lipid oxidation rates also increase with increasing pH in Tween 20-stabilized oil-in-water emulsions (Huang et al., 1996; Mancuso et al., 1999).

**Table 1. Ferrous Iron Concentration Remaining 2 min after Addition to SDS-Stabilized Hexadecane Emulsions Containing either 0 or 1.8 mM Cumene Peroxide at pH 3**

| | 0 mM cumene peroxide | 1.8 mM cumene peroxide | | |
|---|---|---|---|---|
| $Fe^{2+}$ added | 0.5 | 0.5 | 1.0 | 2.0 |
| $Fe^{2+}$ concn (mM) at 2 min | 0.51 ± 0.01 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.11 ± 0.01 |

**Oxidation of Ferrous Iron.** Table 1 shows that when 0.5 and 1.0 mM $Fe^{2+}$ were added to an SDS-stabilized hexadecane emulsion containing cumene hydroperoxide, all of the $Fe^{2+}$ was oxidized within the first 2 min. When 2 mM $Fe^{2+}$ was added to the emulsion containing cumene hydroperoxide, 0.11 mM $Fe^{2+}$ was still present after 2 min. Fukuzawa and Fujii (1992) found complete oxidation of $Fe^{2+}$ in <1 min in SDS micelles containing linoleic acid hydroperoxides.

**$Fe^{3+}$-Promoted Hydroperoxide Decomposition As Affected by Surfactant Charge and pH.** The effect of 0.5 mM $Fe^{3+}$ on the decomposition of cumene hydroperoxide was studied at pH 3 in SDS-, Tween 20-, and DTAB-stabilized trilaurin emulsions (Figure 3). Only pH 3 was tested due to low solubility of $Fe^{3+}$ at

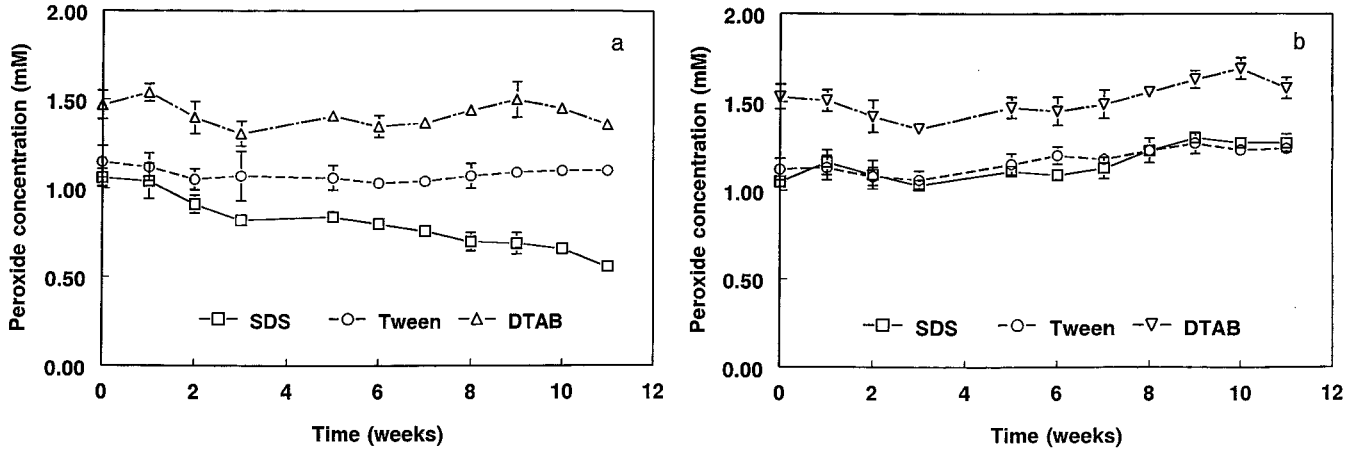


**Figure 4.** Decomposition of cumene hydroperoxide in SDS-, Tween 20-, and DTAB-stabilized hexadecane emulsions at pH 3.0 (a) and 7.0 (b) in the absence of added iron. Emulsions were incubated at 20 °C.

pH 7.0. $Fe^{3+}$ (0.5 mM) caused a gradual decomposition of peroxides in the SDS-stabilized trilaurin emulsion with peroxide concentrations after 24 h of incubation being 86% lower than the control (Figure 3A). $Fe^{3+}$ (0.5 mM) was not able to decompose peroxides in either the Tween 20-stabilized (Figure 3B) or DTAB-stabilized (Figure 3C) trilaurin emulsions.

**Cumene Hydroperoxide Stability in the Absence of Added Iron.** Long-term storage studies of cumene peroxide stability in emulsions stabilized by each of the three different surfactants were carried out without iron added, in the dark, at 20 °C. Lower incubation temperatures were used in the long-term study to minimize evaporation; these lower temperatures necessitated the use of hexadecane. At pH 3, a significant ($p \leq 0.05$) decrease in peroxides was observed in the SDS-stabilized emulsion beginning at 2 weeks (Figure 4a). Peroxide concentration decreased 47% in the SDS-stabilized emulsion after 11 weeks of monitoring, whereas no change in peroxide concentration was observed for the Tween 20- and DTAB-stabilized emulsions during the entire incubation period. There was no significant change ($p \geq 0.05$) in peroxides in any of the emulsions at pH 7.0 (Figure 4b).

**Effect of EDTA and NaCl on Peroxide Decomposition.** EDTA was able to decrease $Fe^{2+}$ (0.5 mM)-promoted cumene peroxide decomposition in SDS-stabilized hexadecane emulsions at pH 3.0 in a concentration-dependent manner (Figure 5). At pH 3, EDTA (2 mM) also inhibited initial decomposition of peroxides by $Fe^{2+}$ in Tween 20-stabilized (Figure 6a) and DTAB-stabilized trilaurin emulsions (Figure 6b). These concentrations of EDTA also inhibited iron-promoted oxidation of corn and salmon oil emulsions stabilized by SDS, DTAB 20, and Brij 35 (Mei et al., 1998a,b).

NaCl can displace iron from the surface of SDS-stabilized emulsions droplets, thus altering iron-promoted lipid oxidation rates (Mei et al., 1998a,b). NaCl (0−170 mM) was only able to inhibit $Fe^{2+}$-promoted cumene hydroperoxide decomposition at 170 mM in SDS-stabilized trilaurin emulsions at pH 3. NaCl (170 mM) decreased peroxide concentration by 16 and 66% after 10 min and 3 h of incubation, respectively, compared to decreases in peroxides of 25 and 86% in the $Fe^{2+}$ control (Figure 7). Lower NaCl concentrations (3−87 mM) did not impact $Fe^{2+}$-promoted peroxide decomposition at pH 3 in SDS-stabilized emulsions. NaCl (170 mM) did not alter the extent of peroxide

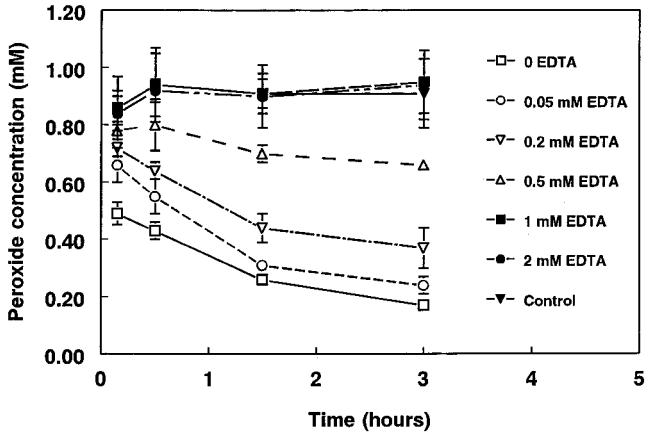


**Figure 5.** Ability of EDTA (0.05−2.0 mM) to inhibit the decomposition of cumene hydroperoxide by 0.5 mM $Fe^{2+}$ in a SDS-stabilized trilaurin emulsion at pH 3.0. Emulsions were incubated at 55 °C.

decomposition in the Tween 20-stabilized (Figure 6a) or the DTAB-stabilized (Figure 6b) trilaurin emulsion. Mei et al. (1998a) found that the addition of 0−173 mM NaCl had no significant influence on the iron-promoted oxidation rates of Tween 20- and DTAB-stabilized corn oil emulsions at pH 6.5 as measured by peroxide value and TBARS.

## DISCUSSION

A major cause of the acceleration of lipid oxidation in foods is formation of free radicals resulting from the reaction of iron with lipid peroxides that are known to exist in unsaturated lipids (Halliwell et al., 1995). In oil-in-water emulsions, aqueous phase transition metals (e.g., iron and copper) are likely to interact with lipid peroxides in the interfacial region that exists between the dispersed oil droplets and the continuous aqueous phase (Coupland and McClements, 1996). Recent studies have suggested that the charge of emulsion droplets impacts the prooxidant activity of iron by altering iron−lipid interactions at the droplet interface (Mei et al., 1998a,b; Donnelly, 1998).

The ability of iron to decompose peroxides in emulsions was determined in a model system consisting of cumene hydroperoxide in hexadecane or trilaurin. The polarity of the lipid phase could impact the reactivity of lipid peroxides by altering the physical location of the

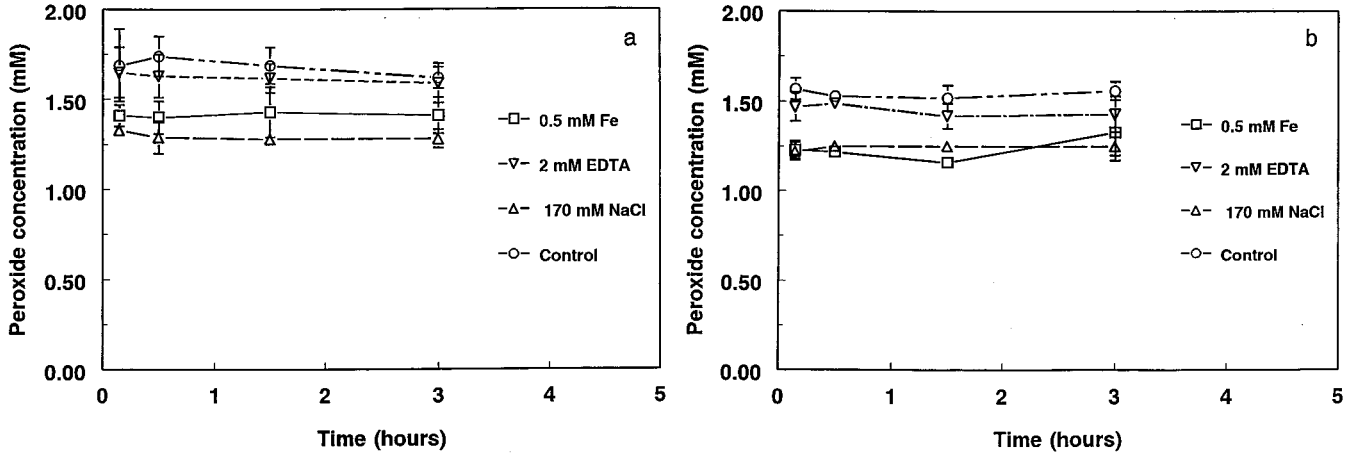


**Figure 6.** Ability of 2.0 mM EDTA and 170 mM NaCl to alter the rate of cumene hydroperoxide decomposition by 0.5 mM $Fe^{2+}$ in (a) Tween 20- and (b) DTAB-stabilized trilaurin emulsions at pH 3.0. Emulsions were incubated at 55 °C.

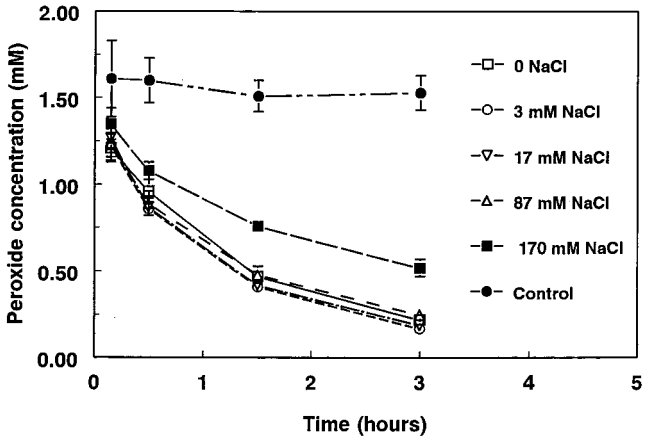


**Figure 7.** Effect of NaCl (3.0−170 mM) on the decomposition of cumene hydroperoxide by 0.5 mM $Fe^{2+}$ in a SDS-stabilized trilaurin emulsion at pH 3.0. Emulsions were incubated at 55 °C.

peroxides in the emulsion droplet (e.g., partitioning of peroxides at the emulsion droplet interface would increase with decreasing lipid polarity). Hexadecane and trilaurin have dielectric constants of approximately 2.0 (Israelachvili, 1992) and 3.0−3.2 (Formo et al., 1979), respectively, indicating that they have similar polarities. No major differences were observed in iron-promoted decomposition of cumene hydroperoxide in these two different lipid systems (Figures 1 and 2), suggesting that hexadecane is a suitable nonoxidizable lipid source to study the reactivity of peroxides in emulsions.

$Fe^{2+}$ (0.5 mM) decomposed cumene hydroperoxide rapidly with significant decreases in peroxides observed in all emulsions after 10 min of incubation (Figures 1, 2, 6, and 7). This initial decrease in peroxides occurred over a similar time period as the disappearance of $Fe^{2+}$ in SDS-stabilized hexadecane emulsions containing cumene hydroperoxide (Table 1). In addition, the initial decomposition of cumene hydroperoxide by $Fe^{2+}$ was greater in SDS- than Tween 20- or DTAB-stabilized emulsions as observed in both hexadecane (Figure 1) and trilaurin (Figure 2). The molar ratios of initial decrease in peroxides to added $Fe^{2+}$ at pH 3.0 and 7.0, respectively, were 1.04 and 1.16 in SDS-stabilized, 0.28 and 0.64 in Tween 20-stabilized, and 0.56 and 0.58 in DTAB-stabilized emulsions droplets. The higher amount of initial peroxides decomposed in the SDS-stabilized emulsion suggests that the $Fe^{2+}$-promoted reaction occurs more rapidly as iron−droplet interactions increase. The fact that $Fe^{2+}$ reacts with peroxides in DTAB- and Tween 20-stabilized emulsions (in which iron−emulsion droplet interactions are expected to be low because there is no strong attraction between iron and the droplet surface) as well as in SDS-stabilized emulsions (in which iron−emulsion droplet interactions are high) suggests that $Fe^{2+}$ is not absolutely required to be electrostatically attracted to the emulsion droplet to react with cumene peroxide due to its high reactivity and solubility. However, this initial decomposition of peroxides by $Fe^{2+}$ could also be due to solubilization of some of the peroxides into the continuous phase and/or in surfactant micelles (surfactant micelles are unlikely in the SDS- and DTAB-stabilized emulsions because initial surfactant concentrations were near the critical micelle concentration) or due to the solubilization of some of the $Fe^{2+}$ into the lipid phase.

Decomposition of cumene hydroperoxide was much greater in the SDS-stabilized emulsions at pH 3.0 in both the presence and absence of added iron (Figures 1, 2, 4, 5, and 7). In addition, $Fe^{3+}$ promoted cumene hydroperoxide decomposition only in SDS-stabilized emulsions at pH 3.0 (Figure 3). The greater instability of cumene hydroperoxide in the SDS-stabilized emulsions at pH 3.0 suggests that both $Fe^{2+}$ and $Fe^{3+}$ are involved in the reaction in a redox cycling pathway because peroxide decomposition continued after $Fe^{2+}$ was completely oxidized (Figures 1A and 2A and Table 1) and decomposition of peroxides by both $Fe^{2+}$ and $Fe^{3+}$ was greater than the original amount of iron added to the system (e.g., molar ratio of peroxide decrease to $Fe^{2+}$ = 2.8 and 2.5 after 3 h in SDS-stabilized hexadecane and trilaurin, respectively; Figures 1A and 2A). This suggests that iron was decomposing peroxides by a redox cycling pathway such as

$$LOOH + Fe^{2+} \rightarrow LO^{\bullet} + Fe^{3+} + OH^{-}$$

$$LOOH + Fe^{3+} \rightarrow LOO^{\bullet} + Fe^{2+} + H^{+}$$

The ability of iron redox cycling to only occur in the SDS-stabilized emulsion at pH 3.0 suggests that the iron (in particular $Fe^{3+}$) must be in close proximity to the emulsion droplet surface for efficient redox cycling to occur (iron−SDS-stabilized emulsion droplet interactions increase with decreasing pH; Mei et al., 1998b) and not simply due to increased iron solubility with

decreasing pH (reactivity of iron was not observed to dramatically increase with decreasing pH in Tween 20- and DTAB-stabilized emulsions, in which iron−droplet interactions are low). Lack of decomposition of cumene hydroperoxide after 10 min of incubation in the DTAB and Tween 20 emulsions is likely due to depletion of $Fe^{2+}$, with the resulting $Fe^{3+}$ being unable to promote peroxide breakdown.

## CONCLUSIONS

Iron-promoted decomposition of lipid peroxides is an important factor in the development of oxidative rancidity. $Fe^{2+}$ is capable of decomposing lipid peroxides in nonionic, cationic, and anionic emulsion droplets, whereas $Fe^{3+}$ decomposes peroxides only in anionic emulsion droplets at pH 3.0. In addition, chelators and NaCl decrease the interaction of iron with anionic emulsion droplets and thus decrease peroxide decomposition. These results further support the hypothesis that factors that increase iron−lipid interactions increase the prooxidant activity iron in oil-in-water emulsions. These results also suggest that when iron−emulsion droplet interactions are high, iron is able to decompose peroxides more efficiently through its ability to redox cycle.

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