Droplet Composition Affects the Rate of Oxidation of Emulsified Ethyl Linoleate

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ABSTRACT: Our objective was to study the influence of droplet composition on the rate of lipid oxidation in emulsions. A series of oil-in-water emulsions stabilized by a nonionic surfactant (Tween 20) was studied. These emulsions had the same total oil concentration (5 wt%) and initial droplet diameter (0.3 μm), but contained droplets with different ratios of ethyl linoleate (substrate) and *n*-tetradecane (inert diluent). Lipid oxidation was measured as a function of time by three different methods: gas-chromatographic determination of residual substrate; ultraviolet-visible spectrophotometric determination of conjugated dienes; and measurement of aqueous thiobarbituric acid-reactive substances. All three methods showed similar trends for emulsions of similar composition. The progress of lipid oxidation in the emulsions was dependent on the concentration of ethyl linoleate in the emulsion droplets. At low concentrations (1% oil as substrate), oxidation proceeded at a relatively slow and constant rate. At intermediate concentrations (20%), the oxidation rate was rapid initially and then slowed down with time. At high concentrations (100%), the oxidation rate was slow at first, and then increased with time. An explanation of our results is proposed in terms of the distribution of substrate molecules between the droplet interior and interface, and the ingress of aqueous radicals into the emulsion droplets. *JAOCS 73*, 795–801 (1996).

KEY WORDS: Emulsions, lipids, micelles, oxidation, rancidity.

Lipid oxidation is of great significance to food scientists because it leads to the generation of unpleasant flavors and aromas ("rancidity"), and to the formation of compounds that may be toxic to human health (1–4). To efficiently control or prevent these undesirable reactions, it is necessary to have a thorough understanding of the factors that influence the radical reaction between oxygen and unsaturated lipid (3,5–7). Indeed, research carried out in this area has already enabled food manufacturers to improve quality and stability of many products by using antioxidants or modified storage procedures.

Most studies of lipid oxidation in foods have been concerned with oxidation of bulk lipids. Nevertheless, many foods are complex multicomponent heterogeneous systems. Foods may contain a huge number of different molecular species, which chemically and physically interact with each other. They may have various levels of structural organization, ranging from the molecular to the macroscopic. In addition, their properties may change with time or in response to alterations in environmental conditions. With the growing emphasis on the development of novel formulated foods, it is becoming increasingly important for the food industry to improve its understanding of the relationship between the physical structure, interactions, and dynamics of the various components in foods and the propensity to undergo lipid oxidation (8).

The lipid fraction of most foods is a complex mixture of compounds, comprised mainly of different types of fatty acids and their glycerol esters (5). Nevertheless, it is only those fatty acids with pentadiene structures that are vulnerable to oxidation under normal storage conditions (5,6). The objective of our study was to investigate the effect that the ratio of oxidizable to nonoxidizable fat has on the rate of lipid oxidation in oil-in-water emulsions.

The inherent compositional and structural complexity of real foods means that systematic studies of lipid oxidation must first be carried out in model systems. These systems should have the basic features of the real system but have well-defined compositions and structural properties. Many of the model systems used by food scientists are similar to those used to study biological systems, where lipid oxidation is also of concern because of the destruction of unsaturated fatty acids in membranes due to singlet oxygen (3). These systems frequently consist of lipids solubilized in surfactant micelles, vesicles, or membranes (9,10). Although these systems do mimic some of the important features of lipid oxidation in food emulsions (e.g., the importance of interfacial reactions), there are other aspects that are not modeled satisfactorily, such as the partitioning of lipid molecules between the interior of a droplet and the interface, or the ingress of radicals into a droplet (8). Consequently, conclusions that are valid for micellar or membrane systems are not directly applicable to emulsions. The most common type of food emulsion consists of tiny oil droplets (typically between 0.1 to 10 μm), dispersed in an aqueous solution (11). Kinetic stability of these systems is achieved by using amphiphilic molecules (either proteins or small-molecule surfactants), which absorb to the surface of a droplet during homogenization and prevent the subsequent coalescence of droplets.

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Much of the early work on lipid oxidation in emulsion systems did not take into account the structure of the system, i.e., droplet size distribution, interfacial properties (12,13). This was largely due to the lack of suitable instrumentation for physical characterization of emulsions at that time. Nevertheless, this early work highlighted many of the important factors that affect lipid oxidation in emulsions, such as oxygen pressure, temperature, pH, and substrate type (6,12,13). Recently, a number of workers have studied the relationship between lipid oxidation and the physical structure of oil-in-water emulsions. The effectiveness of antioxidants in bulk and emulsified oils has been compared (14,15). Paradoxically, it was observed that nonpolar antioxidants are more effective in aqueous based oil-in-water emulsions, whereas polar antioxidants are more effective in bulk oils (14). This has been attributed to the tendency for the antioxidant molecules to accumulate at the droplet interface and form a protective layer around the lipid. It has been shown that increasing the viscosity of the aqueous phase of safflower oil emulsions by adding sugars reduces the lipid autoxidation rate (16), presumably by reducing the rate of oxygen diffusion in the aqueous phase. Based on these results, it is not unreasonable to suggest that radicals, generated in the aqueous phase (which most commonly occurs in food processing operations), must move into an emulsified oil droplet before lipid oxidation can be initiated. Further evidence for the importance of interfacial reactions on lipid oxidation is seen in the synergism between water- and oil-soluble antioxidants, e.g., ascorbic acid (a water-soluble antioxidant) acts primarily to regenerate oxidized α-tocopherol (17) (an amphiphilic antioxidant)—presumably by interfacial reaction.

Recently, it has been shown that the addition of emulsified hydrocarbon droplets to an aqueous solution of surfactant micelle systems that contain an oxidizable substrate retards the rate of oxidation (18,19). This is presumably because some of the substrate diffuses into the emulsion droplets and is therefore less susceptible to oxidation than when it is solubilized in surfactant micelles; alternatively, some of the measured oxidation markers may have dissolved in the oil droplets, causing them to become less detectable to the analytical methods used.

In the present work, we show that the proportion of oxidizable lipid in an emulsion droplet affects its oxidation kinetics, and we suggest how this may be attributed to the physical distribution of the reacting species in the droplets.

MATERIALS AND METHODS

All reagents were supplied by Sigma Chemical Company (St. Louis, MO). No additional purification was undertaken of any reagents. Each experiment was replicated at least once and showed a high degree of reproducibility.

Emulsion preparation. The aqueous phase used to make up the emulsions consisted of 2 wt% Tween 20 (polyoxyethylene sorbitan monolaurate, a nonionic surfactant) dispersed in 50 mM, pH 7.0 sodium phosphate buffer. Oil phases were prepared by mixing different proportions of ethyl linoleate (substrate) and *n*-tetradecane (diluent). Emulsions were prepared by homogenizing 5 wt% of the oil phase with 95 wt% of the aqueous phase by using high-powered ultrasound (Braun Sonic-U, 10–60 s, maximum power; Curtis-Matheson, Cincinnati, OH). Each emulsion is subsequently referred to according to the percentage of ethyl linoleate in the oil droplets. A "1% emulsion" is therefore actually a 5 wt% oil-in-water emulsion that contains 1 wt% of substrate in the oil droplets (or 0.05 wt% of the total emulsion).

Emulsion characterization. Droplet size distributions were measured by a static light-scattering technique (Horiba LA-700; Horiba Instruments Incorporated, Irvine, CA). This technique measures the angular dependence of laser light scattered by the droplets in an emulsion. A relative refractive index of 1.1 was used by the instrument to calculate the droplet size distributions. The droplets were diluted, so the oil concentration was less than 0.04 wt%, to eliminate multiple scattering effects. The mean droplet diameter of the emulsions is reported as the volume-surface diameter: $d_{32} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$, where n_i is the number of droplets with diameter d_i. The degree of emulsification was varied, so that the initial $d_{32} = 0.30 \pm 0.03$ μm. A typical droplet size distribution is shown as Figure 1.

Emulsion storage conditions. Aliquots (5 mL) of each emulsion were mixed with small volumes of freshly prepared iron/ascorbic acid mixture (final concentrations: [$FeSO_4$] = 40 μM; [L-ascorbic acid] = 200 μM) and shaken (0–44 h, at 37 ± 2°C). Aliquots of these emulsions (2.5 mL for the 1% emulsions, 0.5 mL for the others) were withdrawn at measured intervals, placed in sample vials, and then stored frozen (at −20°C) until required for analysis.

Lipid extraction from emulsions. Solvent (*iso*-propanol: *iso*-octane, 50% vol/vol) was added to the sample vials (15

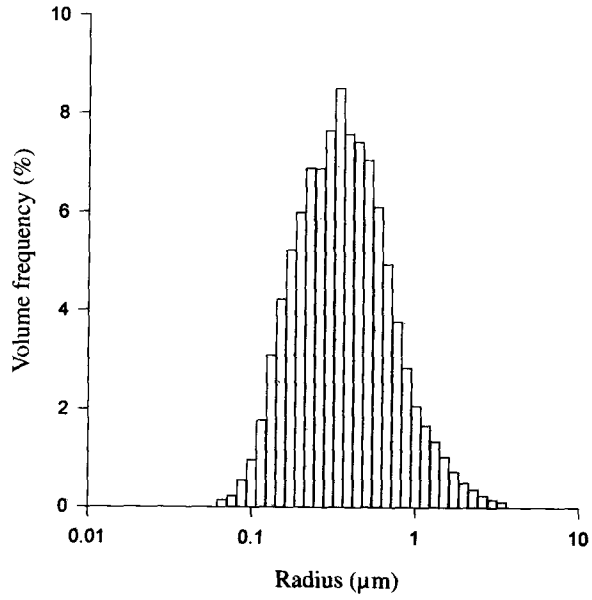

FIG. 1. Typical emulsion droplet size distribution.

mL for the 1% emulsions, 3 mL for the others). Hydrochloric acid (6 N, two drops) was added, and each sample was thoroughly mixed. The acid facilitated separation of the organic and aqueous phases. Aliquots (0.6 mL) of the aqueous phase were retained for thiobarbituric acid-reactive substances (TBARS) analysis (see below). The organic phase was extracted with twice its volume of distilled water, the two phases were separated by centrifugation, and aliquots of the organic phase were retained for further analysis.

Conjugated dienes determination. Methyl palmitate (150 μg) was added to an appropriate volume of organic extract as an internal standard, so that the ethyl linoleate in the control samples was 150–200 μg. The volume was made up to 5 mL with *iso*-octane and thoroughly mixed. The absorbance (A_{235}) was measured against an *iso*-octane blank in a λ3 spectrophotometer (Perkin–Elmer Co., Oak Brook, IL). After analysis, samples were stored (−20°C) prior to further analysis.

Residual substrate determination. Samples prepared for the conjugated diene determination were directly injected into a Hewlett-Packard 5890 gas chromatograph (Hewlett-Packard, Avondale, PA), fitted with a Supelcowax 10 column (Supelco, Bellefonte, PA) (30 m, 0.32 mm i.d, 0.25 μm film) and an HP 3920 integrator. The flow conditions are set out as follows. Gas: 100 mL min^{-1} He; column temperature program: 150 to 245°C at 2.5°C min^{-1}; injector temperature: 250°C; detector: flame-ionization detection, 275°C. These conditions gave clear resolution of the ethyl linoleate and methyl palmitate from other peaks. The amount of substrate (ethyl linoleate) in each sample was measured against the internal standard (methyl palmitate). The reported residual substrate was calculated relative to the amount present in the control (time 0) samples, which were defined as 100%.

TBARS determination. Antioxidant solution (2 drops, 3% butylated hydroxyanisole, 3% butylated hydroxytoluene, 54% propylene glycol, 40% Tween 20) was added to the aliquots (0.6 mL) of the aqueous emulsion extract. TBA solution (2.00 mL, 1% 4,6-dihydroxy-2-mercaptopyrimidine in 0.075 N NaOH), HCl (4.00 mL, 0.12 N), and water (5.00 mL) were added, and the tubes were sealed and heated (100°C, 30 min), then rapidly cooled in cold water. If the samples were turbid, aliquots (5 mL) were mixed with trichloromethane (2 mL) and centrifuged; the absorbance of the upper layer was measured at 532 nm. Otherwise, the samples were measured directly.

RESULTS

All oxidation measurements are reported as a percentage of the initial amount of substrate present in the droplets, and are therefore relative indicators of oxidation. The actual amount of material oxidized was higher in the emulsions that contained the greatest initial concentration of ethyl linoleate, although the relative amounts varied.

Effect of droplet composition. Residual ethyl linoleate and conjugated dienes formed were measured at 4, 24, and 44 h of incubation for a range of droplet compositions (Figs. 2 and 3, respectively). In the initial stages of oxidation (4 h), the rate of oxidation is most rapid in the emulsions with intermediate concentrations of ethyl linoleate (20–40%), as suggested by the greatest loss of substrate (Fig. 2) and formation of conjugated dienes (Fig. 3). After 24 h, this effect is still clearly seen, but after 44 h lipid oxidation in the droplets with high concentrations of substrate is the greatest. These results clearly demonstrate that the rate of lipid oxidation in emulsions depends on the droplet composition, but not in a simple fashion. Our results suggest that varying the concentration of

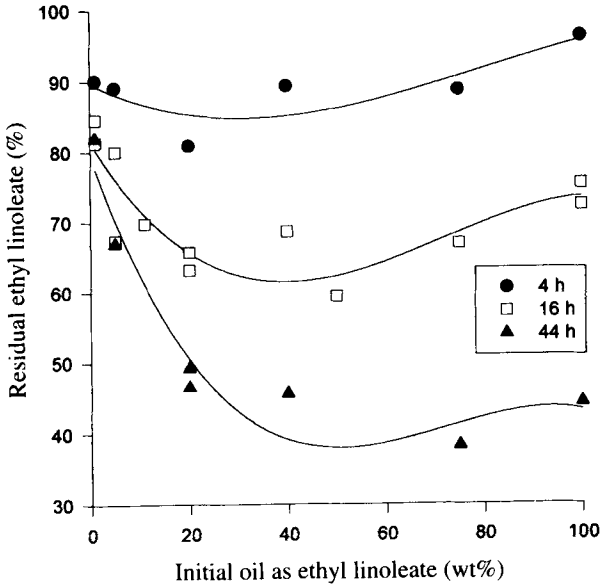

FIG. 2. Loss of ethyl linoleate for a range of emulsion droplet compositions after three storage times.

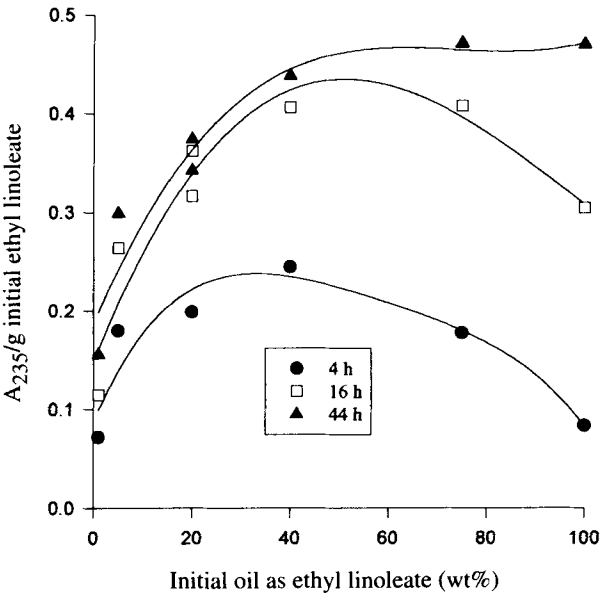

FIG. 3. Formation of conjugated dienes for a range of emulsion droplet compositions after three storage times.

substrate in the droplets gives three types of oxidation kinetics: (i) low substrate concentrations (< 20%)—slow oxidation; (ii) intermediate substrate concentrations (*ca.* 20–40%)—initially rapid, slowing later; and (iii) high substrate concentrations (>40%)—initially slow, becoming faster later.

Kinetic studies. Three droplet compositions, 1, 20, and 100% ethyl linoleate, were selected as representative of the oxidation occurring in each of the kinetics types. The time dependence of lipid oxidation in emulsions that contained droplets of these compositions was then studied over a two-day period (Figs. 4–6). The results of these kinetic studies confirmed our earlier observations.

The rate of loss of ethyl linoleate from the 1% emulsions is the slowest observed, and proceeds at an approximately constant rate over 44 h. The 20% emulsion shows a rapid initial loss of substrate, which becomes slower with time. The 100% emulsion (droplets containing pure substrate) shows a relatively slow initial rate of loss of ethyl linoleate, which increases later. The proportion of ethyl linoleate destroyed is equal for the 20 and 100% emulsions after *ca.* 38 h.

The formation of conjugated dienes with time in the 1% emulsion is relatively slow compared to the other emulsions (Fig. 5). In the 20% emulsion, the reaction products were formed rapidly in the initial stages of the experiments, but later slowed down and then reached a constant level after approximately 24 h. The 100% emulsions showed a relatively slow rate of conjugated diene formation initially, which increased after about 10 h. The proportion of initial substrate converted to conjugated dienes was equal for the 20 and 100% emulsions after approximately 24 h.

Conjugated dienes are products formed relatively early in the course of lipid oxidation; TBARS are formed from the breakdown of intermediate compounds and are a measure of degraded substrate. Water-soluble TBA-reactive aldehydes were determined kinetically for 20 and 100% emulsions to provide further evidence of the effect of droplet composition on the course of ethyl linoleate oxidation (Fig. 6). Measurements could not be made on the 1% emulsions because the absolute amount of substances formed was too low to accurately detect. Again, we observed that the 20% emulsion

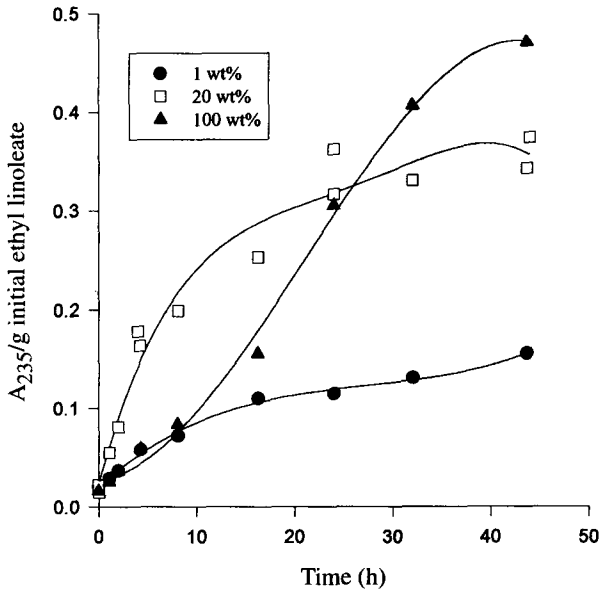

FIG. 5. Formation of conjugated dienes with time for three emulsion droplet compositions (ethyl linoleate/total oil).

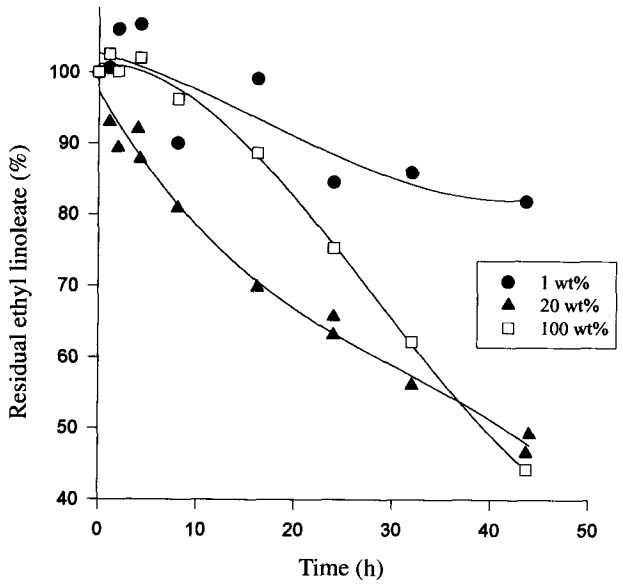

FIG. 4. Loss of ethyl linoleate with time for three emulsion droplet compositions (ethyl linoleate/total oil).

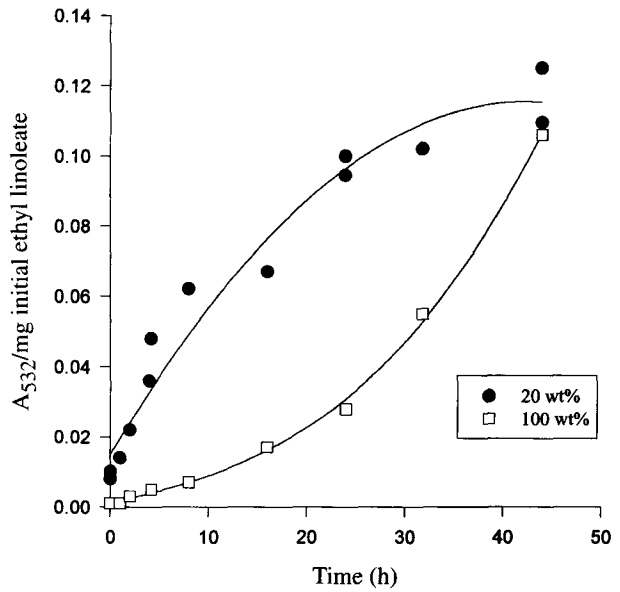

FIG. 6. Formation of water-soluble thiobarbituric acid-reactive substances with time for two emulsion droplet compositions (ethyl linoleate/total oil).

showed an initially rapid increase in concentration of oxidation product that slowed with time, while the 100% emulsion is initially slow and becomes more rapid at longer times. The amount of TBARS formed per unit of initial substrate would probably cross just after 44 h.

DISCUSSION

In an attempt to explain our measurements, we considered the physical mechanisms that occur during the lipid oxidation process. The iron/ascorbate system generates highly polar radicals in the aqueous phase, e.g., $O_2^{\bullet -}$ and $OH^{\bullet}$. The ethyl linoleate is contained within the emulsion droplets, and so we must assume that initiation takes place when a radical collides with an emulsion droplet, penetrates the membrane, and encounters a substrate molecule near the droplet surface. Once initiation has occurred, the lipid radicals generated interact with other substrate molecules and dissolved oxygen to propagate the oxidation reaction. The *n*-tetradecane molecules are not susceptible to oxidation under the conditions used in our experiments and therefore act as an inert diluent. Their presence in the droplets could affect lipid oxidation by influencing both the initiation and propagation steps.

Initiation. The rate of initiation depends on the ease at which the radicals generated in the aqueous phase can interact with the substrate molecules at the oil–water interface. One would therefore expect that the rate of initiation would depend on the concentration and molecular orientation of the substrate molecules at the interfacial region. If ethyl linoleate and *n*-tetradecane had the same surface activity, one would expect the concentration of substrate in the interfacial region to be the same as that in the interior of the droplet. In this case, the relative rate of initiation (initiation rate per unit mass of substrate) would be independent of the ethyl linoleate concentration. Actually, ethyl linoleate is more surface-active than *n*-tetradecane because it is unsaturated and contains carbonyl groups. For this reason, it is more likely to accumulate at the interface than hydrocarbon molecules. Nevertheless, a droplet has a finite surface area, and once it has been saturated with ethyl linoleate molecules, the concentration at the surface cannot increase any further. Thus, at low substrate concentrations, one would expect a greater percentage of the substrate molecules to be located at the droplet surface.

To obtain a rough idea of the concentration of substrate required to saturate the surface of the emulsion droplets, we assumed that all of the ethyl linoleate molecules present in a droplet are at the surface (Fig. 7B), i.e., ethyl linoleate is completely surface-active. That is to say, each droplet consists of a sphere of *n*-tetradecane molecules (radius R) inside a shell of ethyl linoleate molecules (internal radius R, external radius $R + r$, where r is shell thickness). The mass fraction, ϕ_M, of ethyl linoleate required to saturate the interface can then be calculated from this geometry according to the following equation:

$$\phi_M = \rho_i[(R + r)^3\text{-}R^3]/[\rho_i\{(R + r)^3\text{-}R^3\} + \rho_d R^3] \quad [1]$$

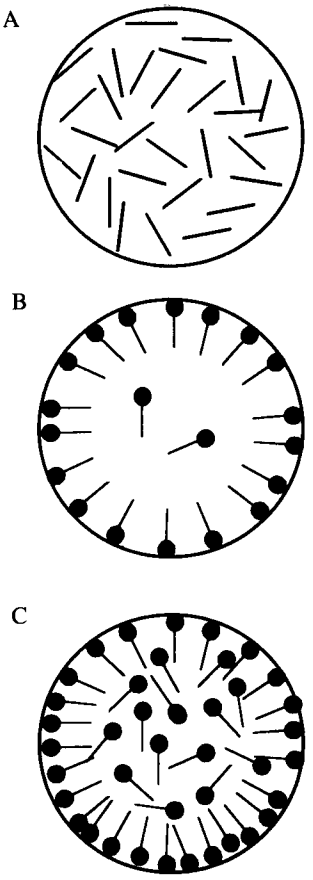

FIG. 7. Diagrammatic representation of the distribution of surface-active or completely oil-soluble solute in an emulsion droplet. Hydrophilic portions of the solute are shown as ●, surface inert parts as —, oil molecules are omitted for clarity; diagram not to scale (typical droplet diameter 300 nm, solute molecule length 2.5 nm). A: Surface-inert substrate randomly distributed in the droplet interior. B: Dilute surface-active substrate mainly accumulated at the interface. C: Concentrated surface-active material: the interface is saturated, so most of the solute accumulates in droplet core.

where ρ_i and ρ_d are the densities of the interfacial region (ethyl linoleate = 892 kg m^{-3}) and the interior of the droplet (*n*-tetradecane = 763 kg m^{-3}). The droplets used in our experiments had a radius of approximately 0.15 μm (R), and the length of the ethyl linoleate molecules is about 2.5 nm (r) (20). Therefore, this equation can be greatly simplified by making use of the fact that $r << R$:

$$\phi_M = 3\rho_i r/\rho_d R \quad [2]$$

Thus, we calculate the concentration of ethyl linoleate at saturation to be approximately 6 wt%. This indicates that, for completely surface-active substrate molecules, all ethyl linoleate present in a droplet would be at the interface up to substrate concentrations of about 6 wt%. Once this value is exceeded, any additional substrate molecules are located in the droplet interior, and would therefore be inaccessible to direct reaction with radicals generated in the aqueous phase. In practice, it is unlikely that the ethyl linoleate molecules are

completely surface-active, and one would therefore expect that saturation would occur at a somewhat higher substrate concentration.

An additional contributing factor to the initiation step is that the orientation of substrate molecules at an interface also depends on their concentration. At low concentrations, ethyl linoleate molecules can orientate themselves so that the hydrocarbon chain lies parallel to the droplet surface (21), thus exposing the pentadiene group to the radicals in the aqueous phase. At higher concentrations, the substrate molecules are forced to pack more tightly together, so that the hydrocarbon tails are perpendicular to the interface and thus less exposed to the radicals. In conclusion, we can say that the greater surface activity of ethyl linoleate molecules, and their consequent concentration at the interface, suggests that the rate of initiation should be greater for droplets that contain low concentrations of substrate, i.e., concentrations less than the saturation packing of substrate molecules at the droplet surface.

Propagation. Once lipid oxidation has been initiated at the interface of a droplet, the nonpolar radicals diffuse into the interior of the droplets. Lipid oxidation then can be propagated by the radicals by abstracting electrons from neighboring molecules on collision, or terminated by interaction with a second radical species. At low concentrations of ethyl linoleate, most of a radical's collisions will be with inert diluent molecules, and propagation will proceed slowly; while in more concentrated systems, a radical is more likely to interact with oxidizable substrate and propagate the oxidation reaction. The same is true for nonradical intermolecular interactions important in oxidation. Thus, the rate of propagation is therefore likely to increase as the concentration of ethyl linoleate in the droplets increases. Oxygen is considerably more soluble in oil than in water (*ca.* 0.6 and 0.2 mM, respectively, at 25°C) (3,22). As the actual molar amount of oxidation is relatively low in the present work, oxygen concentration is unlikely to limit the reaction kinetics. In some industrial treatments of food emulsions, oxygen concentration may be reduced by interactions with food components or by processing (e.g., active metabolic enzymes, heating); under these conditions, different kinetics may be observed.

The inert diluent has two opposing effects on the rate of lipid oxidation in oil-in-water emulsions. The rate of initiation should increase as the concentration of ethyl linoleate in the droplets decreases because a greater percentage of the substrate is at the interface and therefore available for reaction with the radicals generated in the aqueous phase. On the other hand, the rate of propagation should decrease as the concentration of ethyl linoleate in the droplets decreases because the probability of collisions between oil-soluble radicals is reduced.

We attempted to verify this hypothesis by measuring the oxidation of solutions of ethyl linoleate in *n*-tetradecane (Figs. 8 and 9). These bulk oil systems were shaken constantly, so the interface was constantly renewed and surface-active material could not accumulate. Oxidation measurements were made similar to those described above. Because

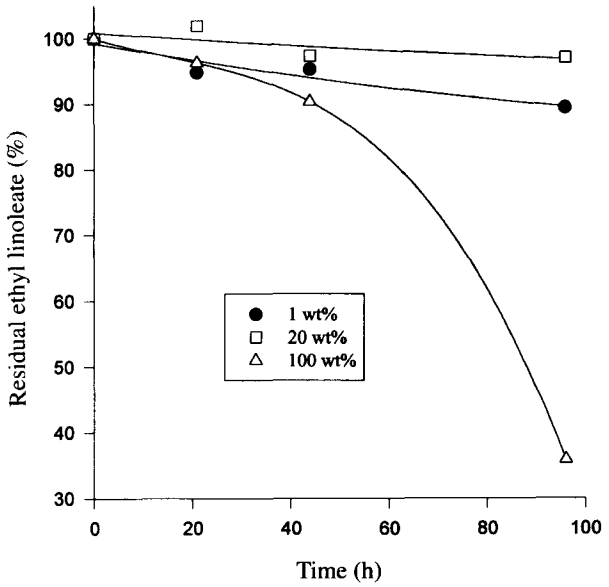

FIG. 8. Loss of ethyl linoleate with time for three bulk oil mixtures (ethyl linoleate/total oil).

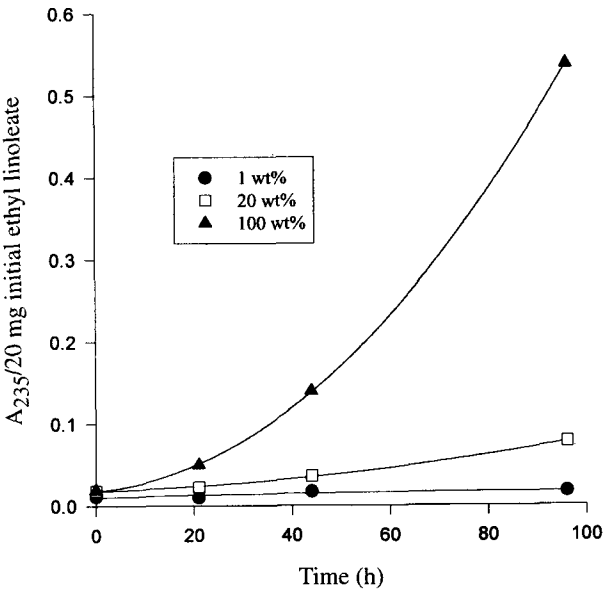

FIG. 9. Formation of conjugated dienes with time for three bulk oil mixtures (ethyl linoleate/total oil).

the catalyst used is water-soluble, it was omitted. Both oxidation markers measured increased similarly with time. The dilute oils (1 and 20%) oxidized only slowly with time, whereas the pure ethyl linoleate reacted initially slowly but much more rapidly at later times. This is consistent with dilute oils oxidizing slowly because of inefficient propagation, as suggested above. However, in the pure oil systems, they do not initially rapidly oxidize because there is no "surface accumulation" effect.

The mechanism proposed above qualitatively accounts for our experimental observations. At low substrate concentrations, the initiation process is rapid, but the propagation step is so slow that it is rate-limiting, and so the overall oxidation rate is slow. At high substrate concentrations, the initiation step is relatively slow but the propagation step is fast, which accounts for the observation that the rate of lipid oxidation is slow in the initial stages, but increases at longer times. At intermediate concentrations, the rate of initiation is still fairly high, and the rate of the propagation step is also fairly high. Thus, there is a rapid initial rate of oxidation but a slower rate at longer times, compared to the 100% emulsion in which the propagation step is more important. The changing importance of these factors as oxidation proceeds is seen in the times when the degree of oxidation of the 100% emulsion surpasses the 20% emulsion, i.e., 25, 39, and *ca.* 45 h for conjugated dienes, residual substrate, and TBARS, respectively.

Based on our analysis, we predict the following general phenomena will be true for the oxidation of lipids in food emulsions: (i) Changes in particle size will only affect oxidation kinetics when the change allows a higher proportion of the oxidizable material to accumulate at the interface. This effect will be seen most clearly in the early stages of oxidation. (ii) The greater the surface activity of the substrate molecules the more likely they are to be at the droplet interface and therefore the greater the oxidation rate. (iii) Increasing the radical generation rate will have the most pronounced effect on the early stages of oxidation when initiation processes are dominant.

Our experiments clearly show that the ratio of oxidizable to nonoxidizable compounds in emulsion droplets affects the rate at which lipid oxidation proceeds. This may have important consequences for many real food systems, which contain varying proportions of saturated and unsaturated molecules. We propose a physical mechanism to account for our observations; it assumes that initiation occurs at the droplet interface and that the concentration of substrate at the interface depends on its surface activity. This is a simple model, but it is a first step toward understanding the complex phenomenon of lipid oxidation in emulsions. A more sophisticated model would have to take into account the fact that the physicochemical properties of the substrate molecules are altered as they are oxidized, i.e., their partitioning between droplet, interface and aqueous regions, and their surface activity. These changes will certainly complicate the oxidation procedure, because the more surface-active reaction products may accumulate at the interface in preference to the original substrate.

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