JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

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Effects of Metal Chelator, Sodium Azide, and Superoxide Dismutase on the Oxidative Stability in Riboflavin-Photosensitized Oil-in-Water Emulsion Systems

JaeHwan Lee[†] and Eric A. Decker*[,‡]

[†]Department of Food Science and Technology, Seoul National University of Science and Technology, Seoul, Korea

[‡]Department of Food Science, University of Massachusetts, Amherst, Massachusetts 01002, United States

ABSTRACT: The effects of riboflavin photosensitization on the oxidative stability of oil-in-water (O/W) emulsions were determined using lipid hydroperoxides and headspace volatile analyses. The influences of a metal chelator, sodium azide, and superoxide dismutase (SOD) on oxidation pathways were tested to gain a better understanding of the role of transition metals, singlet oxygen, and superoxide anion, respectively. Emulsions with riboflavin and visible light irradiation had significantly higher lipid hydroperoxides and volatiles ($p < 0.05$) as compared to samples without light irradiation or riboflavin. The addition of ethylenediammetetraacetic acid (EDTA) decreased the formation of lipid hydroperoxides, hexanal, 2-heptenal, and 1-octen-3-ol in a concentration-dependent manner. Sodium azide, a singlet oxygen physical quencher, only inhibited the formation of 2-heptenal and 1-octen-3-ol. Overall, photosensitized riboflavin participated in both type I and type II pathways in O/W emulsions, and these pathways enhance the prooxidant activity of metals through their ability to produce lipid hydroperoxides and superoxide anion.

KEYWORDS: Riboflavin photosensitization, O/W emulsion, oxidative stability, metal chelators, superoxide anion, singlet oxygen

INTRODUCTION

Oil-in-water (O/W) emulsions are composed of an aqueous continuous phase and emulsifier surrounding dispersed lipid particles with a mean diameter between 0.1 and 100 μm.[1] Lipid oxidation is one of important chemical reactions in foods containing fats and oils during processing and storage. Depending on the food matrix, the major oxidation mechanisms and factors influencing the rates of lipid oxidation are different.[1−3]

In bulk oil systems, the degree of unsaturation in triacylglycerols as well as other minor constituents of oils including amphiphilic compounds and moisture contents affects oxidative stability during autoxidation.[3,4] Free fatty acids (FFA), monoacylglycerols, diacylglycerols, phospholipids, and oxidized lipid products are some of the reported amphiphilic compounds found in crude and refined vegetable oils.[3]

Lipid oxidation in O/W emulsions take places at the interface of the lipid and aqueous phases.[1,3] Interaction between lipid hydroperoxides and transition metals at the droplet surface has been proposed as one of major pathways of lipid oxidation in O/W emulsions. Therefore, the presence of antioxidants and chelating agents, interfacial and droplet characteristics, and ingredient interactions are critical factors influencing the rates of lipid oxidation in O/W emulsions.[1,5,6]

Light irradiation is one of key oxidation mechanisms involved in the oxidation of food lipids. Ultraviolet irradiation can accelerate the rates of lipid oxidation through the generation of free radicals in oils.[2,7,8] Although unsaturated fatty acids do not absorb the energy of visible light,[7] irradiation with visible light in the presence of photosensitizers such as chlorophylls and riboflavin can accelerate lipid oxidation greatly in oils and dairy products, as well as model systems containing FFAs.[9−12]

Mechanisms of photosensitized oxidation can be explained by type I and/or type II pathways depending on the types of photosensitizers and conditions of oxidation environments. The singlet state photosensitizers can absorb visible light energy and become excited to their singlet state. The excited singlet state photosensitizers may change into the excited triplet state photosensitizers by intersystem crossing mechanisms. The excited triplet state photosensitizers can abstract electrons or hydrogen atoms from substrates to generate radicals (type I pathway) or transfer its energy to triplet oxygen to form singlet oxygen (type II pathway) depending on the solubility and availability of triplet oxygen and substrates.[13,14] Superoxide anion can be formed through type II pathway at relatively lower rates than singlet oxygen.[15]

Although many studies have been conducted to understand the factors influencing the oxidative stability in O/W emulsions in the absence of light, the effects of riboflavin photosensitization and related factors on the oxidative stability in O/W emulsion systems are rare in the literature. Therefore, the objectives of this study were to determine the effects of riboflavin photosensitization on the lipid oxidation in O/W emulsions and to monitor the effects of a transition metal chelator (ethylenediammetetraacetic acid, EDTA), a physical singlet quencher (sodium azide), and an enzyme capable of specifically inactiving superoxide anion (superoxide dismutase, SOD) on the oxidative stability of O/W emulsion containing photosensitized riboflavin.

Received: February 7, 2011
Accepted: May 4, 2011
Revised: April 28, 2011
Published: May 04, 2011

dx.doi.org/10.1021/jf2001537 | *J. Agric. Food Chem.* 2011, 59, 6271–6276

MATERIALS AND METHODS

Materials. Riboflavin, Tween 20, ferrous sulfate, barium chloride, ammonium thiocyanate, EDTA, sodium azdie, SOD, hexanal, 2-heptenal, and 1-octen-3-ol were purchased from Sigma-Aldrich (St. Louis, MO). The solid-phase microextraction (SPME) fiber of 50/30 μm DVB/Carboxen/PDMS StableFlex was purchased from Supelco, Inc. (Bellefonte, PA). Corn oil was purchase from a local grocery market (Amherst, MA). Hydrochloric acid, other reagent grade chemicals, test tubes, gas chromatography (GC) vials, seals, and septa were obtained from Fisher Scientific (Pittsburgh, PA).

Sample Preparation for the Emulsion and Photosensitized Oxidation. Corn oil and Tween 20 were used for the dispersed phase and emulsifier, respectively, for the O/W emulsion. Tween 20 was added in deionized water at a concentration of 0.25% (w/w) followed by blending in 2.5% (w/w) corn oil for 2 min to form a coarse emulsion using a two-speed hand-held homogenizer (Biospec Products, Inc., Bartlesville, OK). The coarse emulsion was then passed through a APV two stage high-pressure valve homogenizer (APV Americas, Wilmington, MA) at 7000 psi, three times. After the O/W emulsion was prepared, riboflavin was added to the emulsion at 0.13 mM and mixed overnight. Samples without the addition of riboflavin were used as control samples. Samples were stored under visible light irradiation at the light intensity of 1130 lx (Tenmars Electronics Co., Taipei, Taiwan), and lipid oxidation products were measured at 0, 2, 4, 16, and 22 h.

EDTA, a well-known metal chelator, was added to the O/W emulsion containing riboflavin at a concentration of 0.5, 5.0, and 50 mM. Sodium azide, a singlet oxygen physical quencher,[9] was added at a concentration of 0.11, 1.1, and 11.0 mM, while SOD was added at a concentration of 30, 300, and 3000 units. In these lipid oxidation inhibitor studies, control samples were regarded as samples without the addition of EDTA, sodium azide, or SOD, respectively. Samples were prepared in triplicate.

Lipid Hydroperoxides. Lipid hydroperoxides were determined according to the previous report.[6] A 0.3 mL of sample was mixed with 1.5 mL of isooctane/2-propanol (3:2, v:v), vortex-mixed three times for 10 s each, and centrifuged for 2 min at 2000*g*. The upper layer of 0.2 mL was collected and mixed with 2.8 mL of methanol/1-butanol (2:1, v:v). Thirty microliters of thiocyanate/Fe^{2+} solution was added to the mixture and vortex-mixed for 10 s. The thiocyanate/Fe^{2+}solution was made by mixing equal volume of 3.94 M thiocyanate solution with 0.072 M Fe^{2+} solution (obtained from the supernatant of a mixture of one part of 0.144 M $FeSO_4$ and one part of 0.132 M $BaCl_2$ in 0.4 M HCl). The samples were incubated for 20 min at room temperature, and absorbance at 510 nm was measured using an Ultrospec 3000 pro UV/visible spectrophotometer (Biochrom Ltd., Cambridge, England). The concentration of lipid hydroperoxides was calculated using a cumene hydroperoxide standard curve.

Headspace Volatile Analysis. Headspace volatiles in O/W emulsion samples were determined using a Shimadzu GC-17A gas chromatograph (Columbia, MD) with a flame ionization detector (FID) and a Shimadzu 19395A headspace sampler (Avondale, PA). The solid phase for extracting and concentrating headspace volatiles was a 50/30 μm DVB/Carboxen/PDMS StableFlex fiber. The conditions of the headspace sampler were as follows: headspace volatile extraction temperature, 35 °C; extraction time 7 min; desorption time at GC injection port, 2 min. Volatiles were separated isothermally at 100 °C on an HP methyl silicone (DB-1) fused silica capillary column (50 m × 0.31 mm i.d., 1.03 μm film thickness). The temperatures of the injector and detector were both 250 °C. The flow rate of helium carrier gas was 1.0 mL/min, and GC was operated in splitless mode. Concentrations were determined from the peak areas using standard curves made from authentic hexanal, 2-heptenal, and 1-octen-2-ol in the same O/W emulsion matrix. Peak areas of hexanal, 2-heptenal, and 1-octen-3-ol were converted to concentrations using $y = 2.859 \times 10^{-5} \times -5.717$ ($R^2 = 0.990$), $y = 3.592 \times 10^{-5}x - 3.684$ ($R^2 = 0.990$), and $y = 4.040 \times 10^{-5}x - 3.157$ ($R^2 = 0.990$), respectively, where x is the peak response from GC-FID and y is the concentration of volatiles in micromole.

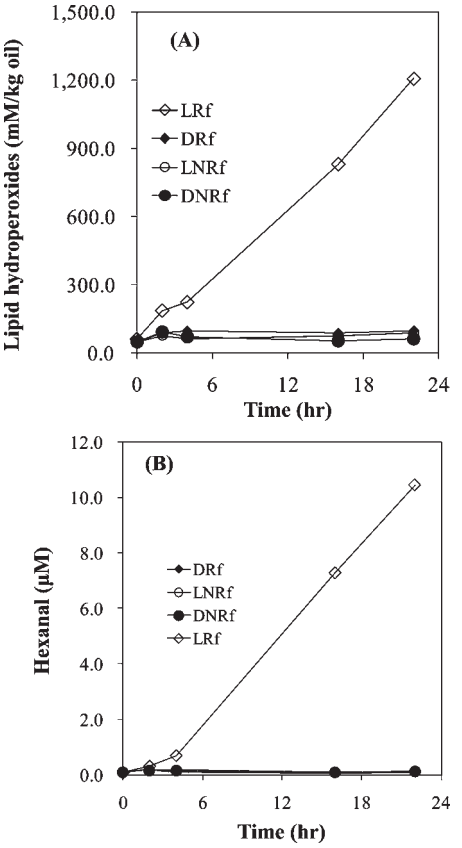

Figure 1. Effect of the addition of riboflavin and visible light irradiation on the changes of lipid hydroperoxides (A) and hexanal (B) in O/W emulsions. LRf, light + riboflavin; DRf, dark + riboflavin; LNRf, light + no riboflavin; and DNRf, dark + no riboflavin.

Statistical Analysis. Data of lipid hydroperoxides and headspace volatiles were analyzed statistically by analysis of variance and Duncan's multiple range test using SPSS software program (SPSS Inc., Chicago, IL). A p value < 0.05 was considered significant.

RESULTS AND DISCUSSION

Riboflavin Photosensitization. The effects of riboflavin and light irradiation on the oxidative stability in O/W emulsion are shown in Figure 1. The samples with addition of riboflavin and light irradiation showed significant increases in lipid hydroperoxides and hexanal as compared to samples without riboflavin, without visible light irradiation or without both riboflavin and light irradiation ($p < 0.05$). Lipid hydroperoxides and hexanal in samples with riboflavin started to increase after 2 h of light irradiation (Figure 1A,B). The results of this study clearly showed that riboflavin photosensitization accelerates the oxidation of lipids in O/W emulsion systems. Riboflavin photosensitization has previously been shown to increase the rates of lipid oxidation in FFAs and oil systems,[9,11,12] and dairy foods including milk[10] and cheese.[16,17] The addition of riboflavin to milk, which is a representative food O/W emulsions, accelerates the formation of volatiles including pentanal, hexanal, heptanal, and dimethyl disulfides.[10]

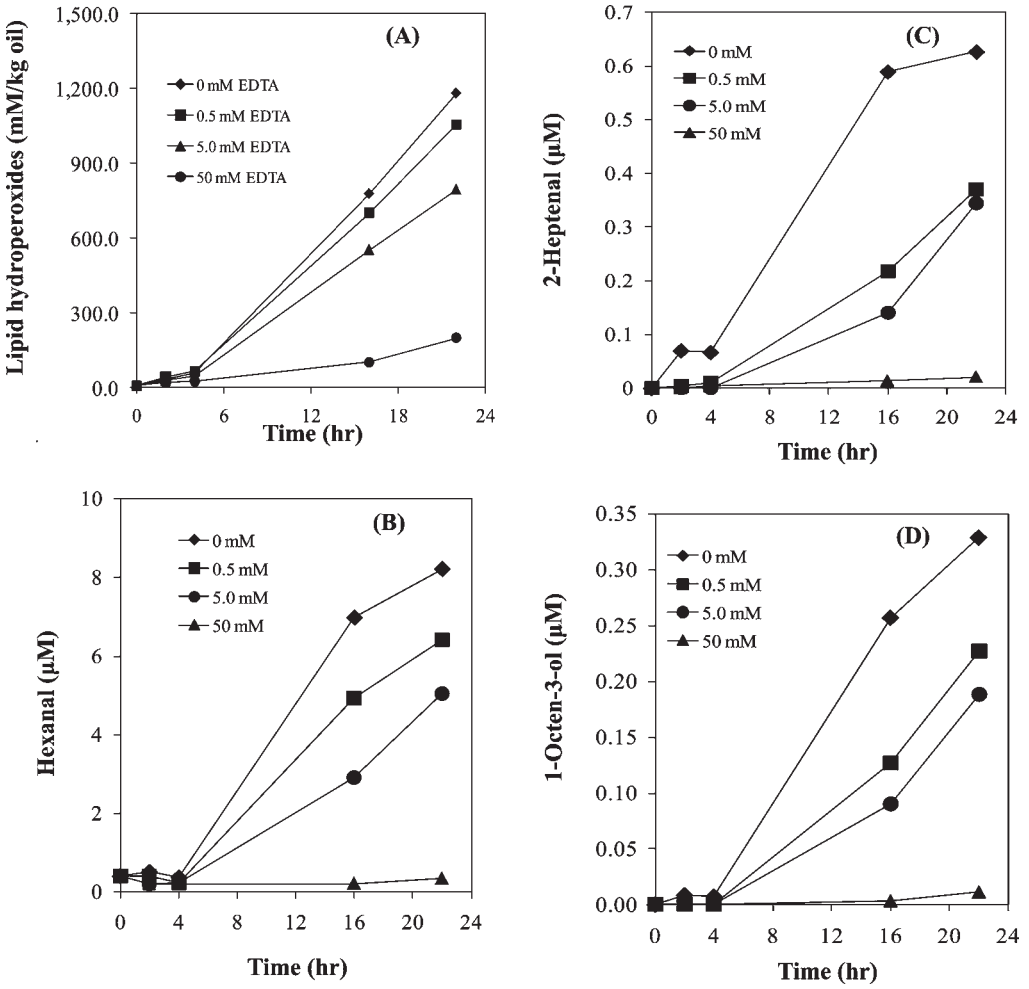

Figure 2. Effect of EDTA (0−50 mM) addition on the changes of lipid hydroperoxides (A), hexanal (B), 2-heptenal (C), and 1-octen-3-ol (D) in riboflavin-photosensitized O/W emulsions.

Factors Affecting Oxidative Stability of Riboflavin Photosensitization. The previous experiment showed that in the absence of the combination of riboflavin and visible light, no detectable lipid oxidation was measured during the 22 h incubation period. Therefore, the subsequent experiments with inhibitors of lipid oxidation were only tested in the O/W emulsions containing riboflavin with light exposure. Transition metals, especially iron, are one of critical factors accelerating lipid oxidation in emulsion systems in the absence of photosensitization.[18−20] For example, metal chelators including EDTA, phytate, and apo-transferrin can enhance the oxidative stability in O/W emulsion by inhibiting the activity of transition metals and/or by facilitating the removal of metal from the emulsion droplet surface.[18−20] The ferrous (Fe^{2+}) ion is more effective than ferric (Fe^{3+}) ion at accelerating lipid oxidation due to higher reactivity and water solubility.

Effects of the metal chelator, EDTA, on the oxidative stability in O/W emulsion systems under riboflavin photosensitization are shown in Figure 2. As the concentration of EDTA increased from 0.5 to 50 mM, oxidation of O/W emulsion under riboflavin photosensitization decreased significantly in a concentration-dependent manner ($p < 0.05$). Results of lipid hydroperoxides (Figure 2A) and all three volatiles including hexanal (Figure 2B), 2-heptenal (Figure 2C), and 1-octen-3-ol (Figure 2D) showed that the addition of EDTA increased the oxidative stability in riboflavin-photosensitized O/W emulsions.

The presence of sodium azide in photosensitized bulk oil systems decreases the rate of oxidation due to the quenching effects of sodium azide on singlet oxygen, which is produced by the type II pathway.[9,21] The effect of sodium azide on the oxidative stability of the O/W emulsion system under riboflavin photosensitization is shown in Figure 3. When lipid oxidation was measured using lipid oxidation products that would be produced in almost all oxidation reactions (e.g., lipid hydroperoxides and headspace hexanal); all concentrations of sodium azide tested had no impact or increased the lipid oxidation in the riboflavin-photosensitized emulsion (Figure 3). When 2-heptenal and 1-octen-3-ol (typical volatiles from singlet oxygen oxidation of linoleic acid) were used to measure lipid oxidation,[21] samples with 1.1 and 11 mM sodium azide decreased lipid oxidation as compared to samples with 0.11 mM sodium azide and control samples (Figure 3C,D). The ability of sodium azide to inhibit the formation of singlet oxygen specific lipid oxidation products implies that singlet oxygen was produced during riboflavin photosensitization. The lack of the ability of sodium azide to inhibit lipid hydroperoxide and headspace hexanal formation could be due to other oxidation pathways occurring at a much faster rate than singlet oxygen, thus masking the singlet

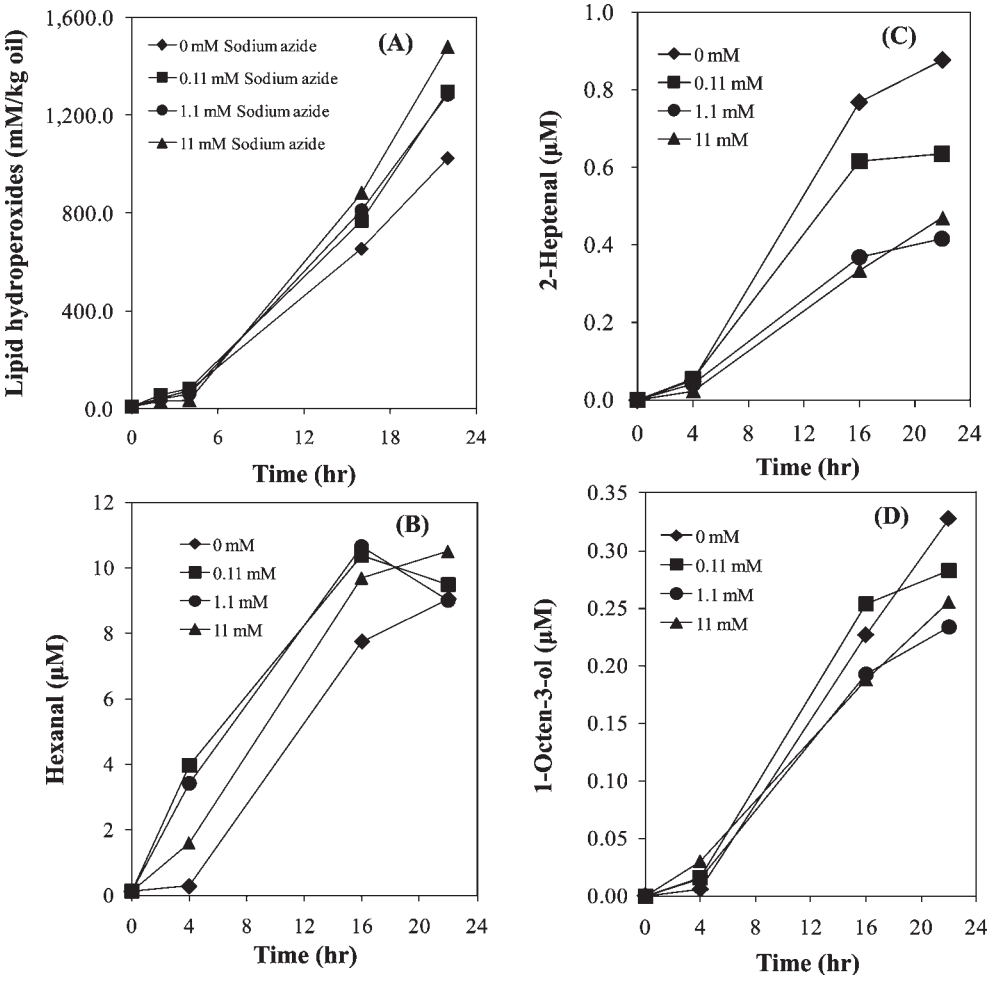

Figure 3. Changes in lipid hydroperoxides (A), hexanal (B), 2-heptenal (C), and 1-octen-3-ol (D) in riboflavin-photosensitized O/W emulsions with the addition of sodium azide (0−11 mM).

oxygen quenching effect of sodium azide. Other studies have shown that sodium azide can quench singlet oxygen in chlorophyll-oxidized linoleic acid,[9] riboflavin-photosensitized milk,[10] and riboflavin-photosensitized mixtures of FFAs.[21]

In the presence of light, riboflavin participates in the type II pathway, which not only produces singlet oxygen but also superoxide anion.[9] Effects of SOD addition on the oxidative stability in O/W emulsion systems under riboflavin photosensitization are shown in Table 1. When lipid hydroperoxides were used to measure lipid oxidation, increasing concentrations of SOD did not show consistent increasing or decreasing trends of the hydroperoxide concentrations. When headspace aldehydes that are produced by metal-promoted hydroperoxide decomposition were used to measure lipid oxidation, maximal inhibition was observed at 30 units of SOD with further increases in the enzyme having no additional impact on oxidation. As with the sodium azide results, these data indicate that riboflavin at least partially participated in the type II pathway to produce superoxide anion as evidenced by the ability of SOD to inhibit photosensitized riboflavin-promoted aldehydes formation in the O/W emulsions.

The ability of EDTA to strongly inhibit lipid oxidation in the presence of photosensitized riboflavin suggests that the prooxidant activity of metals was enhanced by the combination of riboflavin and visible light. In emulsions, transition metals such as iron primarily promote lipid oxidation through the decomposition of lipid hydroperoxides into high energy free radicals.[6,19] Photosensitized riboflavin could increase the prooxidant activity of metals in the type I pathway through the ability of excited riboflavin to abstract hydrogen from the low bond dissociation energy of C−H in unsaturated fatty acids to generate alkyl radical ($L^{\bullet}$), which will react with triplet oxygen to form peroxyl radical ($LOO^{\bullet}$), which in turn can abstract hydrogen from another fatty acid to form a lipid hydroperoxide (Figure 4). Thus, the type I pathway would produce lipid hydroperoxides, the oxidation substrate for transition metals.

Photosensitized riboflavin in the O/W emulsion did not seem to strongly participate in the type II pathway since neither sodium azide nor SOD were strong inhibitors of lipid oxidation. However, this pathway was active and could impact metal promoted lipid oxidation by at least two pathways. First, singlet oxygen produced by the type II pathway can directly react with unsaturated fatty acids to generate hydroperoxides, again producing an oxidation substrate for metals (Figure 4). In addition, superoxide anion produced by the type II pathway could reduce ferric (Fe^{3+}) to the more reactive ferrous (Fe^{2+}) ions, which accelerates the decomposition of hydroperoxides into alkoxyl radical ($LO^{\bullet}$) followed by formation of volatile and nonvolatile lipid oxidation products (Figure 4).

dx.doi.org/10.1021/jf2001537 |J. Agric. Food Chem. 2011, 59, 6271–6276

Table 1. Changes of Peroxide Values, Hexanal, 2-Heptenal, and 1-Octen-3-ol in Riboflavin-Photosensitized O/W Emulsions with the Addition of SOD[a]

	SOD (unit)	0 h	2 h	4 h	16 h	22 h
lipid hydroperoxides (mM/kg oil)	0	8.2 ± 0.4 aA	44.2 ± 4.0 bB	73.0 ± 4.3 cC	733.5 ± 34.4 aD	1103.3 ± 10.1 cE
	30	8.2 ± 0.4 aA	53.9 ± 3.3 cB	83.4 ± 11.7 cC	683.3 ± 29.9 aD	1058.7 ± 25.2 bcE
	300	8.2 ± 0.4 aA	36.8 ± 2.4 abB	60.9 ± 3.5 bC	729.6 ± 10.0 aD	968.9 ± 29.2 bE
	3000	8.2 ± 0.4 aA	27.9 ± 0.7 aB	34.1 ± 3.4 aC	758.1 ± 21.6 aD	893.6 ± 21.0 aE
hexanal (μM)	0	0.13 ± 0.02 aA	–	0.28 ± 0.02 cA	7.75 ± 0.95 aB	9.02 ± 0.51 bC
	30	0.13 ± 0.02 aA	–	0.22 ± 0.01 bA	7.07 ± 0.80 aB	7.38 ± 0.36 aB
	300	0.13 ± 0.02 aA	–	0.33 ± 0.01 dA	6.94 ± 0.77 aB	7.26 ± 0.36 aB
	3000	0.13 ± 0.02 aA	–	0.18 ± 0.01 aA	7.15 ± 0.63 aB	7.28 ± 0.62 aB
2-heptenal (μM)	0	ND	–	0.05 ± 0.01 cA	0.76 ± 0.03 bB	0.87 ± 0.03 bC
	30	ND	–	0.03 ± 0.00 bA	0.61 ± 0.01 aB	0.68 ± 0.03 aC
	300	ND	–	0.03 ± 0.00 bA	0.63 ± 0.02 aB	0.68 ± 0.02 aC
	3000	ND	–	0.01 ± 0.00 aA	0.63 ± 0.02 aB	0.66 ± 0.02 aB
1-octen-3-ol (μM)	0	ND	–	0.006 ± 0.000 bA	0.227 ± 0.017 bB	0.328 ± 0.023 bC
	30	ND	–	0.003 ± 0.001 aA	0.193 ± 0.005 aB	0.276 ± 0.012 aC
	300	ND	–	0.005 ± 0.001 bA	0.209 ± 0.00 aB	0.283 ± 0.004 aC
	3000	ND	–	0.004 ± 0.003 abA	0.195 ± 0.018 aB	0.271 ± 0.025 aC

[a] –, samples were not analyzed. ND, not detected. In the same column, different small letters mean significant differences ($p < 0.05$). In the same row, different capital letters mean significant differences ($p < 0.05$).

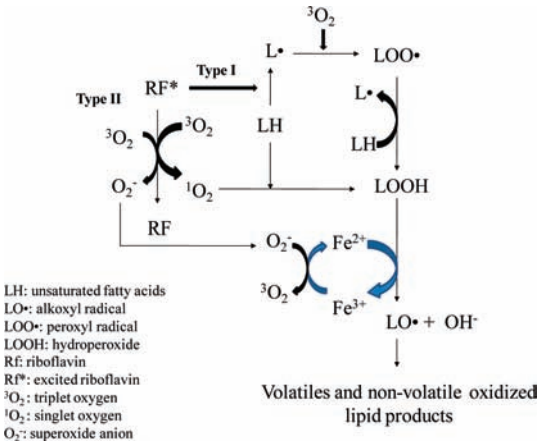

Figure 4. Propose pathways of lipid oxidation in O/W emulsions under riboflavin photosensitization.

The pathways by which photosensitized riboflavin impacts lipid oxidation can be dependent on the food matrix such as bulk oil vs emulsion systems.[1−3] For example, sodium azide was not able to strongly inhibit the formation of lipid hydroperoxides and headspace hexanal, implying that the mechanisms of riboflavin photosensitization and action of sodium azide in O/W emulsion may not be the same as those in bulk oil systems. This could be due to the relatively short shelf life of reactive oxygen species such as singlet oxygen in water.[2] Another example is the impact of photosensitized riboflavin on the oxidation stability of milk where single oxygen seems to play a more important role than in the emulsion system used in this study.[10] This discrepancy could be due to the presence of strong metal chelators in milk such as lactoferrin and casein.[22,23] These chelators would reduce the prooxidant activity of metals, thus making the singlet oxygen pathway more important than metal-promoted hydroperoxide decomposition.

In conclusion, riboflavin photosensitization significantly accelerated the formation of lipid hydroperoxides and volatile compounds in O/W emulsions, presumably through its ability to enhance the prooxidant activity of metals. Both type I and type II pathways of riboflavin photosensitization were involved in promoting lipid oxidation. However, the type I pathway seems to be more important than type II, which may be due to the relatively short shelf life of singlet oxygen and superoxide anion in aqueous environment. However, both pathways are important in their ability to enhance the prooxidant activity of metals through their ability to produce lipid hydroperoxides and superoxide anion. These results suggest that in aqueous-based foods susceptible to the formation of photosensitized riboflavin, antioxidant technologies should include the combination of inhibition of reactive oxygen species as well as prooxidant metals.

AUTHOR INFORMATION

Corresponding Author

*Tel: 1-413-545-1026. Fax: 1-413-545-1262. E-mail: edecker@foodsci.umass.edu.

Funding Sources

This research was conducted through the financial support of the Seoul National University of Science and Technology in South Korea.

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