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Inhibited and non-inhibited lipid oxidation in colloidal solutions: A review

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Abstract:
Fatty acids possess special structural features that allow them to form surfactants. Their weak C–H bonds trigger oxidation by the radical-chain mechanism. As a result, various colloidal solutions develop in aqueous media, and the new conditions affect the mechanism of fatty acid oxidation.

This review summarizes scientific publications on fatty acid oxidation in colloidal systems registered in Scopus and WoS in 2014–2024. It involved articles on the kinetics of fatty acid oxidation in water-lipid colloidal solutions, e.g., emulsions and micellar solutions.

The main stages of lipid oxidation – initiation, continuation, and chain termination – depend on various factors. The oxidation rate can be affected by the composition of the system, oxygen concentration, distribution of the initiator between the lipid or aqueous phases, type of surfactant, and pH. Each of these factors can change the mechanism of radical chain oxidation, thus affecting the shelf-life and quality of food products. The behavior of antioxidants in colloidal solutions differs from that in true solutions. The oxidation rate, the concentrations of various components, and the antioxidant activity in water-lipid solutions can be measured by different methods. These days, machine learning and artificial intelligence predict oxidation rates and assess the properties of antioxidants in various food systems. If combined together, they improve their predictive ability of the oxidation rate of fatty acids in colloidal solutions.

By establishing the mechanism of fatty acid oxidation in colloidal systems, food scientists design the optimal conditions to preserve antioxidants in various foods and increase their shelf-life.

Keywords: Fatty acids, lipid peroxidation, radical chain oxidation, micelles, emulsion, antioxidants

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INTRODUCTION

Fatty acids are among the most crucial food components. They are essential for human and animal nutrition and health. Fatty acids are prevalent in various food products, e.g., nuts, fish, oils, meat, and dairy products [1–5]. The fatty acids found in these foods typically contain 14–22 carbon atoms [6]. Their hydrocarbon chains may be fully saturated, or they may contain 1–6 double bonds (usually in the *cis*-configuration), with a bis-allylic group between them. Figure 1 illustrates this kind of bond-dissociation energy.

These two structural features lead to two key observations:

1. The structural residues of fatty acids are soluble in organic media, and the presence of easily removable acidic groups provides numerous opportunities for the development of fatty acids-based surfactants, e.g., phospholipids.

2. Weak C–H bonds in unsaturated and polyunsaturated fatty acids facilitate oxidation, thereby reducing the shelf-life of food products.

Considering that many foods that contain water and fatty acids are surfactants, fatty acid oxidation occurs not in their pure form, but rather in colloidal solutions, i.e., emulsions and micellar solutions. Recent reviews [7–10] address the process of fatty acid oxidation in colloidal solutions. However, several unresolved issues remain despite the recent progress in colloidal studies [11]. For example, most reviews fail to consider the instrumental methods for determining oxidation

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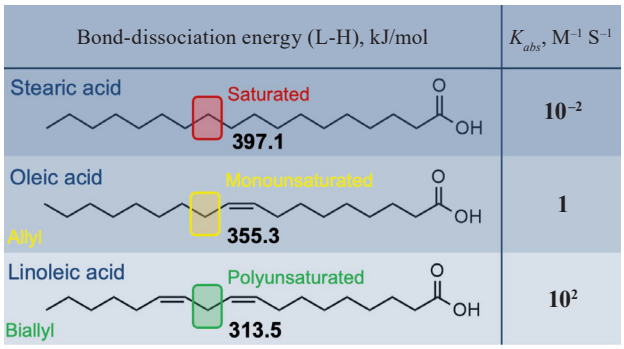

Figure 1 Structures of fatty acids, C–H bond energies, and rate constants for hydrogen abstraction from various functional groups

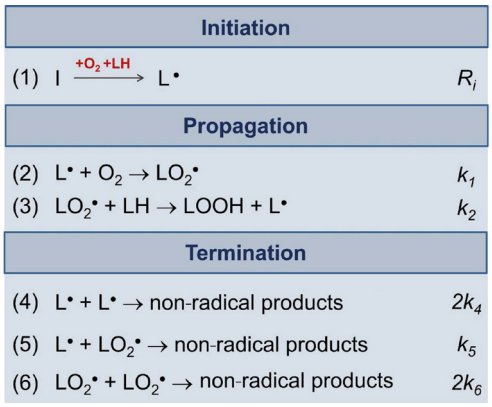

Figure 2 Mechanism of free radical chain oxidation

rates. Such issues as machine learning and artificial intelligence in predicting oxidation rates and inhibitor strengths also remain beyond their scope. Finally, most of them adhere to a strictly phenomenological perspective. This review focuses on examining the kinetics of fatty acid oxidation in colloidal solutions.

STUDY OBJECTS AND METHODS

This review covered publications registered in Google Scholar, ResearchGate, and Scopus in 2002–2023, with the focus on original studies published within the last 10 years in peer-reviewed sources. The search involved such keywords as *lipids oxidation*, *lipid oxidation in emulsion*, *lipid oxidation in micelles*, *antioxidants in emulsion*, and *machine learning lipid peroxidation*. Priority was given to articles published in specialized journals on the kinetics of radical chain reactions and food chemistry.

RESULTS AND DISCUSSION

General issues of fatty acid oxidation. Oxidation mechanisms in colloidal solutions may differ significantly from those in true solutions: their mechanisms are more complex (Fig. 2).

The mechanism of fatty acid oxidation in true solutions is a variety of the free radical chain oxidation mechanism. It closely resembles the oxidation of hydrocarbons (Fig. 2) [12] and is identical for saturated fatty acids. At high oxygen concentrations (~ 10^{-3} M), the likelihood of Reactions 4 and 5 is virtually zero, as the rate of Reaction 1 is close to the diffusion rate [13]. The system contains almost no free alkyl radicals (L•). Consequently, the oxidation rate R_{O_2}, mol/(L·s)) (can be described by Eq. (1) [14]:

$$R_{O_2} = \frac{k_2}{\sqrt{2k_6}}[\mathrm{LH}]\sqrt{R_i} \quad (1)$$

where k_n is the rate constant for the n-th reaction (Fig. 2), L/(mol·s); [LH] is the substrate concentration, mol/L; R_i is the initiation rate, mol/(L·s). The chain propagation is the rate-limiting step in free radical chain processes. Notably, the rate constant k_2 for fatty acids is an additive function of the bis-allylic and allylic groups [15, 16], as illustrated by Eq. (2):

$$k_2 = 4k_a + 2nk_{ba} \quad (2)$$

where is the rate constant for the abstraction of a hydrogen atom from the allylic group, L/(mol·s); is the rate constant for the abstraction of a hydrogen atom from the bis-allylic group, L/(mol·s). Considering that k_a is much lower than k_{ba}, the greatest contribution comes from the bis-allylic groups. Thus, oxidation proceeds in a co-oxidation mode. The oxidation rate can be reduced by increasing the concentration of allylic groups. In [17], diluting fish oil with oleic acid-rich sunflower oils decreased the oxidation rate. Another method to reduce the oxidation rate involves protecting bis-allylic groups by replacing hydrogen with deuterium [18–21]. These substances proved effective antioxidants in model systems, as well as inhibitors of oxidative stress and related pathologies in biological systems [22, 23]. However, these substances are relatively expensive dietary supplements [24], and their effects on the body remain understudied and questionable [25].

Oxygen is another important component that affects oxidation. At high oxygen concentrations, the oxidation rate follows Eq. (1). At low oxygen concentrations, Reactions 4 and 5 are also possible, and the oxidation rate exhibits a more complex dependence [26–28], as illustrated by Eq. (3):

$$\frac{[\mathrm{O_2}]}{[\mathrm{LH}]}\left(\frac{R_\infty^2}{R_{O_2}^2}-1\right)=\frac{k_2k_5}{k_1k_6}+\frac{k_2^2k_4}{k_1^2k_6}\frac{[\mathrm{LH}]}{[\mathrm{O_2}]} \quad (3)$$

where R_∞ is the oxidation rate calculated using Eq. (1); R_{O_2} is the oxidation rate at a specific oxygen concentration, mol/(L·s); $[O_2]$ is the oxygen concentration, mol/L. Since the oxygen concentration in water is approximately an order of magnitude lower than in organic solvents [29], a high-water content in a water/oil system significantly reduces the overall oxygen concentration. Unfortunately, scientific literature rarely provides data on the effect of oxygen concentration on the oxidation rate of fatty acid derivatives [30]. The oxygen concentra-

tion within a micelle depends on the surfactant concentration [31], and the surface area does not affect the rate of oxygen diffusion into the micelle [32].

Additionally, oxygen participates in autoxidation. The rates of auto-initiation are as low as ~ 10^{-8} mol/(L·s) at 70°C and can often be neglected. These processes combine two reactions [33], as illustrated below:

$$LH + O_2 \rightarrow L^{\bullet} + HO_2^{\bullet}$$
$$2LH + O_2 \rightarrow 2L^{\bullet} + H_2O_2$$

The mechanism of this third-order reaction apparently consists of two stages: first, a substrate-oxygen complex develops; second, it is attacked by a substrate molecule. From a chemical kinetics perspective, it is a relatively rare termolecular reaction.

Thus, autoxidation produces not only fatty acid radicals but also the hydroperoxyl radical ($HO_2^{\bullet}$) and hydrogen peroxide. Interestingly, polar solvents increase the rate of auto-initiation [33, 34] and reduce the proportion of termolecular reactions. This effect can be attributed to the disruption of the pre-reaction complex, which decreases the likelihood of the slow termolecular reaction. In this respect, the kinetics of fatty acid oxidation in polar organic solvents requires further research. The formation of $HO_2^{\bullet}$ was also reported in [35], which examined the inhibition of autoxidation in various foods containing fatty acid residues by superoxide dismutase. Additionally, superoxide dismutase inhibited the oxidation of fish oil emulsions [36], indicating the formation of $HO_2^{\bullet}$. The same authors determined that catalase also reduces the oxidation rate [37], which indirectly supports the formation of $HO_2^{\bullet}$ during oxidation because catalase decomposes hydrogen peroxide.

As indicated in the previous paragraph, oxidation may trigger the formation of $HO_2^{\bullet}$ radicals. Only one research featured the rate constant for the reaction of hydrogen atom abstraction from fatty acids by the hydroperoxyl radical [38]: it was approximately 10^3 L/(mol·s) for the bis-allylic group, while allylic groups did not react with $HO_2^{\bullet}$. Additionally, trans-isomers of linoleic acid also did not react with $HO_2^{\bullet}$ [39]. For liquid-phase reactions, all other publications primarily include rate constants for the addition to the double bonds of certain vinyl compounds [40–42], the dependency of rate constants on solvent polarity [43–45], and the reactivity of some inhibitors with $HO_2^{\bullet}$ [46, 47].

Initiation in multiphase systems. The rate of auto-initiation is negligible for the kinetics of fatty acid oxidation. As a result, special initiators are needed to enhance the oxidation process. They can be water-soluble, e.g., AAPH, AMEP, SOTS-1; lipid-soluble, e.g., AIBN, AMVN, and Fenton-like or enzymatic catalysis, e.g., xanthine oxidase-xanthine [48–56]. In all the cases, the position of the initiator influences both the oxidation rate and its mechanism (Fig. 3).

From a kinetic perspective, the decomposition of hydroperoxides is a chain-branching event. This decomposition occurs relatively slowly and is accelerated by temperature or light [57]. Metal ions with variable valency may initiate the oxidation of lipoproteins in emulsions. Iron and copper ions are the most popular ones [58–61]. Yet, the initiation rate depends on multiple factors, such as pH or chelating agents. When studying oxidation kinetics with other types of initiation, this reaction is usually eliminated as an additional source of chain branching. For instance, solutions are prepared using deionized water, and further purification is achieved with ion-exchange resins.

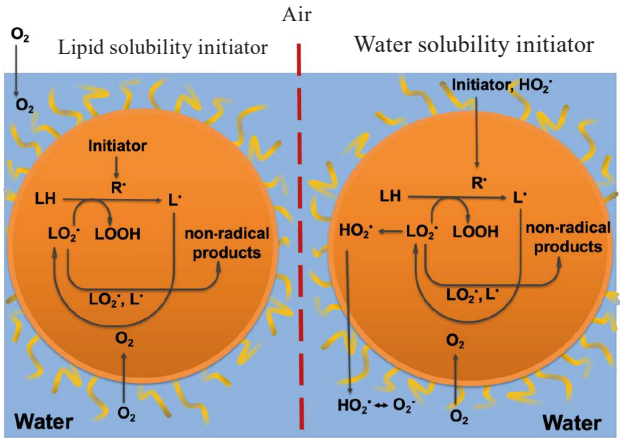

Figure 3 Reaction mechanisms in the presence of water-soluble and lipid-soluble initiators

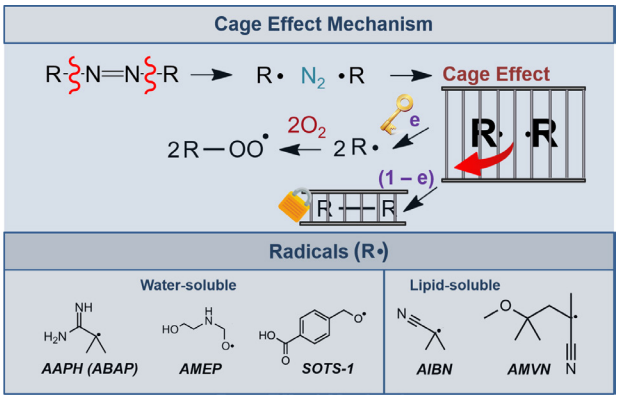

Figure 4 Radical formation during azo-initiator decomposition

Surfactants are often used to form micelles and emulsions, except when the oxidation substrate itself acts as a surfactant, e.g., phospholipids [62]. As a rule, it is either non-ionic or anionic surfactants. Cationic surfactants, however, can degrade the formed hydroperoxides, leading to chain branching [63–66].

Hydroperoxides decompose under the effect of a magnetic field generated by cationic surfactants [67].

Water-soluble initiators are the most popular variant for initiation in micelles, e.g., AAPH (Fig. 4). In this case, the initiation rate depends on pH. At low pH, the initiation rate is higher than at neutral pH, and it is similarly elevated at high pH. The increased initiation rate at low pH is attributed to the additional protonation in the diamine fragment, which enhances the

Coulomb interactions and increases the likelihood of the initiator cage exit [49].

SOTS-1 is a special case [51]. Upon decomposition in water, it generates a superoxide radical. To generate $O_2^{\bullet-}$ (superoxide), it needs an enzymatic system of xanthine oxidase and hypoxanthine [68].

Lipid-soluble initiators are primarily used in emulsions and occasionally in micelles. However, the rate constants for initiation in micelles differ significantly from those in true solutions. For instance, k_i(AMVN) is 2.5×10^{-7} s^{-1} [54], while the rate constant for decomposition is 5.4×10^{-6} s^{-1} [14]. Thus, the likelihood of the radical escaping from the micelle is only about 0.05. In our previous work [69], we observed that it happens because:
– the micelle forms a secondary cell, within which the probability of the radical escaping is significantly lower;
– the lower concentration of oxygen promotes chain termination via Reaction 5 (Fig. 2), which is thermodynamically more favorable than Reaction 6 (Fig. 2).

Interestingly, the rate constant k_i for the lipid-soluble AIBN depends on pH, even though it is within the micelle. The publication in question provided no explanation for this observation, which means that inhibition methods for micellar solutions require further clarification.

Chain propagation. Measuring the rate constants for chain propagation under colloidal conditions is quite challenging. One of the few experimentally determined rate constants for the chain propagation of linoleates in bilayers was found to be several times lower than in true solutions: 16.6 and 70 L/(mol·s), respectively [70]. This result was attributed to the peroxyl radical being "somewhat expelled outward" [48]. In molecular dynamics simulations, the peroxyl radical is more favorably positioned within the lipid region while the hydroperoxide aligns with the aqueous phase [71].

For water-soluble initiators, the "loading" of the micelle is a factor that affects the rate of chain propagation [72, 73]. At 2–20 nm, the oxidation rate exhibits a linear dependence on the number of fatty acid molecules within the micelle. Such sizes allow for the containment of a relatively small number of molecules (up to several hundred), which limits the oxidation rate. Conversely, oxidation in water/oil systems with a droplet size of hundreds of nanometers is much closer to ideal solutions [74]. Similar conclusions were reported in [75] concerning the oxidation of olive oil and fish oil emulsions in water with sizes ranging from 80 to 1300 nm. The lipid oxidation rate in emulsions actually decreased as the droplet size went up [76].

Figure 5 illustrates the mechanism of decomposition hydroperoxyls in micelles. When using water-soluble initiators, some chains in micelles may be propagated by the hydroperoxyl radical ($HO_2^{\bullet}$) [77]. Its presence in the oxidation process of methyl linoleate and methyl linolenate was detected using superoxide dismutase, which converts $HO_2^{\bullet}$ into hydrogen peroxide [78]. For the monounsaturated ester (methyl oleate), the authors observed no superoxide dismutase inhibition, which means that oleate oxidation did not produce $HO_2^{\bullet}$. However, superoxide dismutase inhibition confirms only the cases where $HO_2^{\bullet}$ is both generated and propagates the chain. Remarkably, $HO_2^{\bullet}$ was unable to propagate chains in saturated and monounsaturated fatty acids [38, 39]. Additionally, $HO_2^{\bullet}$ did not participate in chain propagation for linoleates where hydrogen was replaced with deuterium at the bis-allylic position [39].

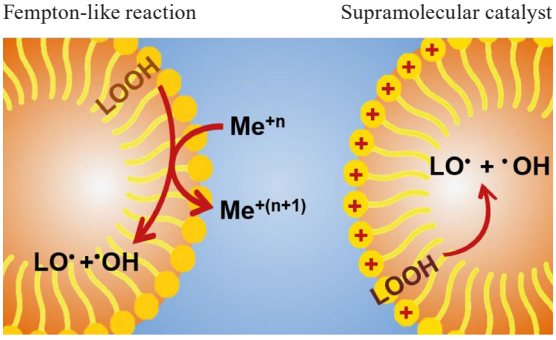

Figure 5 Mechanism of decomposition hydroperoxyls in micelles

A more accurate method for detecting $HO_2^{\bullet}$ described in [79] involved a combination of superoxide dismutase and nitroxide radicals. Nitroxide radicals appeared in the presence of $HO_2^{\bullet}$, but the presence of superoxide dismutase reduced the concentration of $HO_2^{\bullet}$ and shortened the induction period. This method was found lacking because nitroxide radicals were weak antioxidants, which resulted in a poorly defined induction period. Another confirmation of $HO_2^{\bullet}$ formation was the decreased induction period of nitroxide radicals during the oxidation of methyl linoleate in Triton X100 micelles in heavy water [80]. Heavy water led to the replacement of $HO_2^{\bullet}$ with $DO_2^{\bullet}$, which cannot regenerate nitroxide radicals [47, 81].

As for lipid-soluble initiators, the formation of $HO_2^{\bullet}$ did not occur in Triton X100 micelles [69]. It happened because peroxyl radicals are more likely to be destroyed inside the micelle. However, the number of fatty acid molecules inside the micelle interior is limited. When initiated with water-soluble initiators, the chain length exceeded the number of molecules inside the micelle [79]. This phenomenon can partly be explained by the formation of $HO_2^{\bullet}$, but even with the introduction of superoxide dismutase, the chain length remained greater than the number of molecules inside the micelle [79]. Thus, some chains can be transferred through collisions between two micelles, one of which contains a radical [9, 73, 82].

Such chain propagation mechanisms as radical diffusion into the solution and co-oxidation with surfactants [83] are virtually impossible. In the first case, the solubility of fatty acid radicals in aqueous media is minimal. In the second case, it primarily affects hydrophilic regions that do not interact with the micelle interior. However, some non-ionic surfactants, e.g., Triton X100, Tween 65, and Pluronic F68, could undergo oxidation [83, 84]. Thus, we can only discuss parallel oxidation of surfactants and fatty acids.

Chain termination in true solutions occurs via Reactions 4–6 (Fig. 2). At high oxygen concentrations, Reactions 4 and 5 can be neglected since the concentration of alkyl radicals is extremely low. Since the oxygen concentration in an aqueous medium is almost an order of magnitude lower than in organic solvents, Reactions 4 and 5 predominate during chain termination in the micelle. Chain termination is most likely to occur inside the micelle because the concentration of radicals in the organic phase is much higher than in the aqueous phase.

No consensus has been reached so far on the type of chain termination in micellar solutions. AAPH demonstrates both mixed and linear chain terminations. Linear termination might be related to the fact that only one initiator radical enters the micelle whereas quadratic termination requires two chains. In [85], linear termination was explained by the formation of the hydroperoxyl radical: upon exiting the micelle, it converts into a less reactive superoxide anion radical:

$$O_2^{\bullet-} + H^+ \leftrightarrow HO_2^{\bullet} \ (pK_a = 4.8)$$

However, these processes do not terminate the chain but rather slow it down and eventually lead to chain transfer, as evidenced by the higher oxidation rates observed under nanoheterogenous conditions.

The decay of $HO_2^{\bullet}$ in aqueous environments can occur through two reactions [86, 87]:

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + {}^1O_2$$
$$k = 8.3\times10^5 \text{ L/(mol·s)}$$

$$HO_2^{\bullet} + O_2^{\bullet-} + H_2O \rightarrow H_2O_2 + O_2 + OH^-$$
$$k = 9.7\times10^7 \text{ L/(mol·s)}$$

These reactions have high-rate constants, but under neutral pH conditions, the concentration of $HO_2^{\bullet}$ is low, and the chain termination is minimal. In organic solvents, the rate of chain termination depends on the formation of the $HO_2^{\bullet}$-solvent complex [45]. This conclusion for $HO_2^{\bullet} + HO_2^{\bullet}$ was reported in studies that featured rate constants in various solvents.

Loshadkin *et al.* [84, 88–90] explained the gradual increase in the oxidation rate by "radical accumulation". This effect is likely caused by the presence of antioxidant impurities, as evidenced by the increased reaction order with respect to the initiator during the reaction and the longer induction period with decreased initiation rates. Therefore, thoroughly purified reagents are crucial for more accurate kinetic models of lipid oxidation.

Studying chain termination with lipid-soluble initiators is challenging because their concentration is difficult to vary: a lower initiator concentration decreases the already low oxidation rate while a higher concentration may complicate its solubility in micelles.

Inhibited oxidation. Oxidation is often an undesirable process. Equation (1) clearly demonstrates that the oxidation rate can be reduced by decreasing the chain propagation rate (Reaction 2, Fig. 2), by slowing down the initiation rates, or by hydroperoxide decomposition. The types of inhibitors for optimal lipid oxidation are listed below [91]:

– chain-breaking inhibitors that react with peroxyl radicals, e.g., aromatic amines and phenols;
– chain-breaking inhibitors that react with alkyl radicals, e.g., nitroxyl radicals; and
– metal deactivators for variable valency metals.

For metal deactivators, the rate of oxidation initiated by variable valency metal ions depends on pH and the presence of chelating agents, such as EDTA [92]. Acidic pH is known to reduce the rate of oxidation initiated by iron ions. Such surfactants as Tween can also form chelate complexes. Such amino acids as L-lysine and L-asparagine develop complexes with iron ions [93], thereby reducing the oxidation rate in meat products. Sodium citrate additives also reduce oxidation rates [94]. Conversely, monovalent salts tend to increase the oxidation rate, probably due to their impact on the surface of emulsion droplets. Phosphate groups [95], e.g., in sodium caseinate [96], reduce oxidation rates by forming complexes. Buffer solutions based on citrates and phosphates lower oxidation rates by stabilizing iron ions in the solution [97]. An innovative approach to creating new inhibitory materials involves the complexation of variable valency metal ions with poly(hydroxyethyl acrylate) [98]. This method provides coatings for poly(ethylene terephthalate) containers, which extends the shelf-life of food products.

Chain-breaking inhibitors that react with alkyl radicals are generally less effective due to the relatively low concentration of alkyl radicals. The most common inhibitors are various nitroxyl radicals, such as TEMPO and its derivatives. However, they are primarily utilized as radical traps and spin labels in oxidation kinetics (Fig. 6) [39, 79, 99–103]. In practice, the antioxidant action of nitroxyl radicals is not limited to reactions with alkyl radicals [104] because nitroxyl radicals exist as alkoxyamines and hydroxylamines in aqueous environments [105, 106]. Hydroxylamines are particularly strong inhibitors. Nitroxyl radicals also react with $HO_2^{\bullet}$, and this reaction regenerates nitroxyl radicals, facilitating the formation of antioxidant systems. For instance, Amorati *et al.* [47, 107, 108] proposed an antioxidant system based on nitroxyl radicals and 1,4-cyclohexadiene

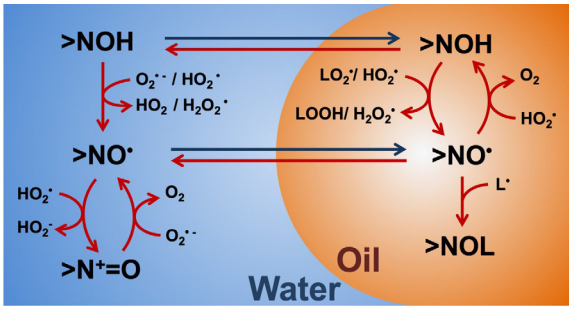

Figure 6 Mechanism of nitroxyl radical-inhibited oxidation of methyl linoleate in micelles (Adapted from [99])

and its derivatives, where $HO_2^•$ is produced upon oxidation. Other potential substrates for similar systems include 1,2-disubstituted ethylenes and 1,4-disubstituted butadienes, which also produce $HO_2^•$ upon oxidation [42]. Additionally, $HO_2^•$ can be generated in systems with oxygen peroxide [109]; however, its concentration in the lipid phase is usually minimal.

The most extensive group of oxidation inhibitors consists of those that react with peroxyl radicals. Various polyphenols and phenols (PhOH) are the most popular inhibitors in this category [46, 110]: vitamin E, epicatechins, Trolox, 2,6-di-tert-butyl-4-methylphenol (BHT), etc. [111–114]. Their mechanism of action in nonpolar organic solutions is typically represented as a hydrogen atom transfer:

$$PhOH + LO_2^• \rightarrow PhO^• + LOOH$$
$$PhO^• + LO_2^• \rightarrow NRP$$

Thus, phenols can terminate two oxidation chains. However, numerous side reactions may reduce their effectiveness e.g., autoxidation reactions, reactions between phenolic radicals, etc. In the case of hydrogen atom transfer, the key parameter is the bond dissociation energy of the O–H bond [115]. The lower the bond energy, the more active the inhibitor. At lower bond energies, autoxidation reactions become more favorable, which can lead to a pro-oxidant effect [116, 117].

$$PhOH + O_2 \rightarrow PhO^• + HO_2^•$$

In this case, autooxidation is accelerated due to the catalytic oxidation of phenols in the presence of iron ions [118, 119].

Assessing antioxidant activity by the bond dissociation energy can yield intriguing results: in [120] the authors demonstrated that the C–H bond energy in flavonoids was lower than the O–H bond energy in phenolic groups.

In multiphase systems, the dependence of antioxidant activity on the structure and polarity of inhibitors differs somewhat from that in true solutions (Fig. 7). Among inhibitors of the same class, the most polar phenolic inhibitors exhibit the highest antioxidant activity in true solutions. In water/oil systems, less polar inhibitors are more effective [121]. This phenomenon is known as the polar paradox [122]: nonpolar antioxidants dissolve better on the lipid surface where the primary oxidation processes occur [123]. Clearly, hydrophobicity can be enhanced by increasing the number of hydrophobic groups in the inhibitor molecule. However, the antioxidant activity of inhibitors gradually reaches a limit with the increasing length of the alkyl tail, a phenomenon termed the cut-off effect [124–126].

Some researchers believe that concentration is also important [127, 128]. For instance, they compared the antioxidant activity of epigallocatechin gallate (EGCG) with its lipophilic ester derivative (tetrastearate) in oil. The ester was more effective at lower concentrations whereas epigallocatechin gallate proved more active at higher concentrations. At low concentrations, the effect of solubility in oil predominates over the interfacial phenomena on antioxidant effectiveness. Thus, non-polar antioxidants with better fat solubility are more effective than their polar counterparts while the reverse is true at higher concentrations. As a result, the polar paradox theory is applicable only when the antioxidant concentration exceeds a critical value to let the interfacial phenomena dominate over solubility parameters.

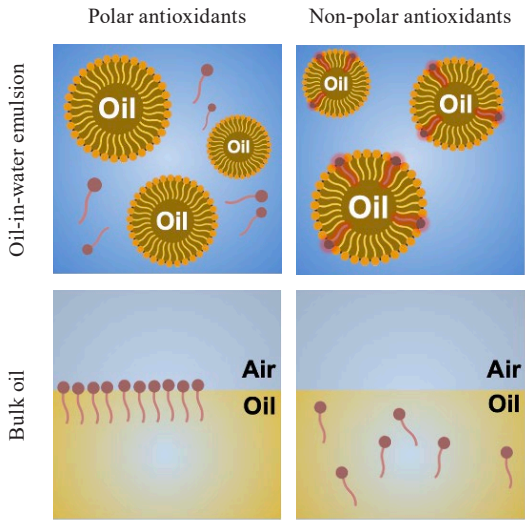

Figure 7 Interfacial phenomena as a possible action mechanism of polar paradox in oil-in-water emulsion and bulk oil

A more complex approach to the effect of the inhibitor at the phase boundary is introduced in [129–131]. For instance, Bravo-Díaz *et al.* [132] developed a pseudophase model: they divided the entire solution into oil, interfacial, and aqueous regions, with surfactants located at the boundary between the lipid and aqueous phases. Each region demonstrated distinct solvent properties and was considered a separate phase, or pseudo-phase. Reagents and other components distributed thermodynamically in line with the Gibbs free energy of transfer. This effect means that the distribution of reagents is always described by partition constants, which remain constant throughout the reaction. Phenolic radicals and their concentration are detected with 4-hexadecylbenzenediazonium, which reacts with phenolates to form colored compounds.

Such polar environments as water or alcohols have a different inhibition mechanism. Previously, polar solvents were believed to reduce the rate of inhibition by forming associates with polar functional groups of inhibitors [133], which required the disruption of hydrogen bonds before the group could react with radicals. Nowadays, there are more complex mechanisms of inhibition in polar media. For example, in medium-polarity environments, e.g., methanol, the preferred mechanism is a single electron transfer-proton transfer (SET-PT) [134]:

$$PhOH + LO_2^• \rightarrow PhOH^{+•} + LO_2^-$$
$$PhOH^{+•} + LO_2^- \rightarrow PhO^• + LOOH$$

Aqueous environments have a tendency to the mechanism of sequential proton loss electron transfer (SPLET) [135–137]:

$$PhOH \rightarrow PhO^- + H^+$$
$$PhO^- + LO_2^{\bullet} \rightarrow PhO^{\bullet} + LO_2^-$$
$$LO_2^- + H^+ \rightarrow LOOH$$

Inhibitors can terminate chain reactions through all three mechanisms, with the sequential proton loss electron transfer predominantly occurring in the aqueous phase, single electron transfer-proton transfer at the interface, and hydrogen atom transfer in the lipid phase. Thus, the effectiveness of antioxidants may vary depending on their location within a multiphase system, with different mechanisms being more favorable in specific regions due to the local environment and solvent properties.

Evaluation of antioxidant activity. Antioxidant activity can be characterized by such parameters as the stoichiometric inhibition coefficient (f) and the chain termination rate constant (k_7). The stoichiometric inhibition coefficient essentially represents the number of broken chains on one inhibitor molecule. For phenols, the most common stoichiometric inhibition coefficient is around 2, but this value may decrease with an increase in the probability of side reactions. Experimentally, the stoichiometric inhibition coefficient f depends on the induction period (τ_{ind}). These quantities correlate as in Eq. (4) [138, 139]:

$$\tau_{ind} = \frac{f[InH]}{R_i} \quad (4)$$

where [*In*H] is the concentration of the antioxidant, mol/L.

The induction period is usually determined by two methods. In line with the geometric method, a tangent is drawn from the section of the exit from the induction period. In this case, the induction period is the intersection of the time axis and the tangent (Fig. 8) [49, 140]. The integral method means that the induction period is calculated as in Eq. (5) (Fig. 9):

$$\tau_{ind} = \int_0^{\infty} \left(1 - \frac{R}{R_0}\right) dt \quad (5)$$

where R is the rate at time t, mol/(L·s); R_0 is the rate of uninhibited oxidation, mol/(L·s).

The chain breakage rate constant k_7 is calculated using Eqs. (6) and (7):

$$F_1 = \ln\left(\frac{1 + R/R_0}{1 - R/R_0}\right) - \frac{R}{R_0} = \frac{k_7 R_0}{fk_2[LH]} t + const \quad (6)$$

$$F_2 = \frac{R_0}{R} - \frac{R}{R_0} = \frac{2k_7 R_0}{fk_2[LH]R_{in}}[InH] \quad (7)$$

In the first case, the dependence of F_1 on time is plotted for the section leaving the induction period. In Eq. (6), the derivative equals,

$$\frac{k_7 R_0}{fk_2[LH]}$$

from which it is easy to calculate k_7. In the second case, the oxidation rate is measured at different inhibitor concentrations, and then a graph of F_2 is plotted against the antioxidant concentration: the resulting derivative reveals the value of k_7. Initially developed for true solutions [141], these approaches are also applicable to colloidal solutions but with some reservations, e.g., the true chain transfer rate constant is unknown.

Measuring the oxidation rate. The oxidation kinetics can be monitored either by the reaction reagents, e.g., oxygen consumption, or by the product accumulation, e.g., hydroperoxides. The antioxidant concentration can be monitored even if oxidation is inhibited. The simplest analysis option is to control the oxygen concentration. One option is to measure the volume of absorbed oxygen [142, 143]. Another one is to determine the concentration of dissolved oxygen in the solution, e.g., with the help of the Clark electrode in aqueous solutions [144]. Photosensors offer a more universal option: they detect singlet oxygen fluorescence [145–148].

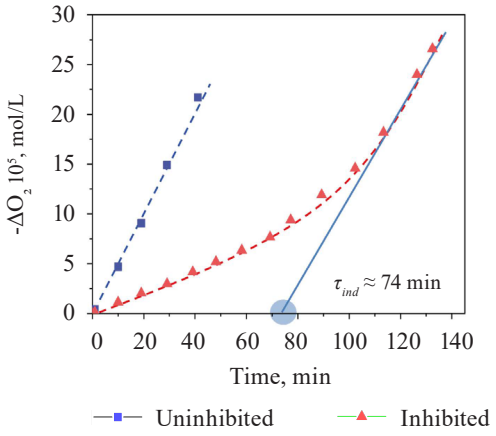

Figure 8 Kinetics of inhibited vs. uninhibited lipid oxidation in micelles

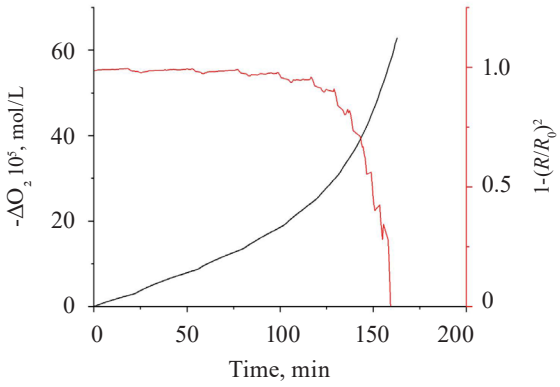

Figure 9 Integral method of determining the induction period

In this case, however, the generation of singlet oxygen may lead to a slight increase in the oxidation rate.

Electrochemical approaches detect oxidation of various species and their oxidation rates. For examples, an amperometric test based on pseudo-titration approach could measure the antioxidant power of wine, orange juice [149], and complex samples [150], such as blood. Voltametric measurements can be applied in a similar way [151]. Other publications report calculating the electrochemical reaction rates based on the Butler-Volmer equation [152, 153].

Recent studies that focus on hydrogen peroxide and hydroperoxide-ion monitor the intra- and extracellular concentration in biological processes by using intermetallic catalytic particles deposited in hydrogel [154] or by applying oxide particles [155] to screen-printed carbon electrode or glassy carbon electrode. The latter option involves electrocatalysis driven by equilibration of Fermi-levels with the surrounding solutions [156, 157]. Highly conductive materials and additives with high specific surface area improve the kinetics of hydroperoxide oxidation and lower the limit of detection in electrochemical methods. The list includes carbon nanotubes, graphene [158], or gold nanoparticles [159, 160].

Since hydroperoxides are subject to decomposition, their accumulation is difficult to monitor directly. Russian researchers prefer this method for determining hydroperoxides that consists of back titration of iodine reduced by hydroperoxide. More complex methods include spectral determination of iodine or iron ions, as well as chromatographic, infrared, and titrimetric determination of triphenylphosphine oxide (TPPO), formed from triphenylphosphine (TPP) [161–171]. However, these methods are not convenient for studying kinetics because they require additional sample processing and a large sample volume for analysis.

Online methods based on high-power laser-irradiation can detect peroxide concentration in the sample. For example, the rapidly developing technique of Raman spectroscopy was applied to oxidation of fat acids and oils, as well as to monitoring reactions in liposomes [172–176]. The fingerprint region (300–1900 cm^{-1}) in Raman spectroscopy [177] is a powerful tool to detect structural changes in compounds, especially

Table 1 Machine learning algorithms in lipid oxidation and stability studies

Prediction	Algorithm	Reference
Evaluate the usefulness of orange by-product flour in the stabilization of oil-in-water emulsions and compare it with purified citrus pectins. Optimize the formulation of emulsion stabilized with orange by-product flour and vegetable proteins, using artificial neural networks	Feed-Forward Backpropagation Network **Input**: orange by-product flour content (0–3.40%) and protein content (0–0.60%) **Output**: emulsion profile (apparent viscosity; d10, d50, and d90 percentiles; ξ-potential; flocculation; creaming index)	[182]
Paired with ATR-FTIR spectroscopy, identify and classify pure njangsa seed oil, palm kernel oil, coconut oil, njangsa seed oil-palm kernel oil, and njangsa seed oil-coconut oil margarine	Support Vector Machines, Decision Tree, Light Gradient-Boosting Machine, K-Nearest Neighbors, Logistic Regression, Random Forest **Input:** FTIR spectra. **Output**: classification of oil.	[183]
Identify off-flavors and compounds of lipid oxidation in dairy powders	Random Forest, Leave-One-Out Cross-Validation, Root Mean Square Error classification of regression **Input:** GC/MS data; sensory data **Output**: Top peak identification, list of compounds	[184]
Define lipid peroxidation activity	Quantitative Structure-Activity Relationship Models **Input:** Top relevant descriptors previously selected by forward stepwise method based on *p*-value criteria **Output:** LP = lipid peroxidation activity/No LP = no lipid peroxidation activity	[185]
Define water and lipid content in emulsion	Self-learning Monte Carlo with Deep Neural Networks **Input:** SWIR spectra **Output:** Water and lipid content	[186]
Measure biorelevance gap in antioxidant assays	Quantitative Structure–Activity Relationship, K-Nearest Neighbors, Support Vector Machine, Bayesian Probabilistic Learning, Random Forest **Input:** Factors governing antioxidant activity *in vivo* **Output**: antioxidation activity of polyphenol	[187]
Detect lipid and protein oxidative damage in thawed pork	Convolutional Neural Network, Multi-Task Convolutional Neural Network **Input:** Raw 1D vis-NIR spectral data at 480–1002 nm **Output**: Malondialdehyde and carbonyl content of samples	[188]
Predicts the antioxidant activity of polyphenols	Neural differential equations **Input:** Concentration headspace hexanal (GC), polyphenols (HPLC) **Output**: Induction period	[189, 190]

in complex composition of many chemical compounds. In this regard, methods of artificial intelligence and chemo-informatics may be useful, too [178]. The technique of Surface Enhance Raman Spectroscopy (SERS) detects lower contents of chemicals with relatively high scattering intensity due to plasmonic resonance and hot-spots between those particles. It proved effective in detecting low concentrations of polyphenols, e.g., chlorogenic acid, caffeic, and gallic acids [179–181]. In addition, SERS-substrates are reusable [176].

Perspectives of machine learning. Predicting lipid oxidation and stability in various systems is a complex process, particularly due to the diverse physicochemical conditions, input data, and algorithms required. Lipid oxidation depends on a number of factors, making it difficult to develop a single, universal algorithm capable of providing accurate predictions across all conditions. Currently, machine learning techniques can predict certain aspects of these systems. For example, such machine learning algorithms as Feed-Forward Backpropagation Networks optimize emulsions stabilized with orange by-product flour (OBPF) and proteins. Support Vector Machines and other models analyze spectroscopy data to classify oils. Deep learning algorithms, such as Neural Differential Equations, perform well in predicting the induction period of polyphenols in bulk lipid oxidation (Table 1).

These models operate on different input data and use various algorithms, such as Random Forest and Convolutional Neural Networks, to address specific challenges, such as predicting lipid content or oxidative damage in meat. Due to the wide range of approaches, a single model may not be sufficient to accurately predict lipid oxidation and antioxidant activity in different systems. As a result, future advancements will likely require new algorithms or combinations of existing ones to improve predictive capabilities across diverse colloidal conditions. An integrated approach is essential for advancing our understanding of lipid oxidation and stability in complex systems.

The prediction of oxidation rate and antioxidant activity often depends on such factors as droplet size, distribution of components between phases, and concentration of components. Components can be split into phases to predict their concentrations using Random Forest and Feed-Forward Backpropagation Network [191]. Since chemical kinetics of oxidation and inhibited oxidation are described by equations, Deep Neural Networks and Neural Differential Equations methods are the most successful methods [192, 193]. The effect of antioxidants on oxidation kinetics can be predicted using Quantitative Structure-Activity Relationship models. Thus, a combination of these three methods (Random Forest/ Feed-Forward Backpropagation Network + Deep Neural Networks/Neural Differential Equations + Quantitative Structure-Activity Relationship) can give an excellent result in terms of predicting the oxidation rate and antioxidant properties.

CONCLUSION

Even though the oxidation of fatty acids in colloid solutions occurs by a radical-chain mechanism, it still depends on the redistribution of components between phases, droplet sizes, oxygen concentration, type of surfactant, and pH. Each of these factors affects the oxidation mechanism.

Unlike oxidation in true solutions, the hydroperoxyl radical is an important oxidation factor in colloidal systems. It participates in the stages of chain propagation and inhibitor regeneration, as well as slows down the chain termination. Apparently, the hydroperoxyl radical is formed from the peroxyl radical in the process of chain initiation.

The role of oxygen concentration remains understudied. Oxidation in water/lipid colloidal solutions occurs with a lack of oxygen, which increases the likelihood of chain termination by the reaction of alkyl and peroxyl radicals.

The study of oxidation kinetics in colloidal solutions requires some caution because unpurified commercial reagents may lead to incorrect conclusions about the oxidation mechanism.

Machine learning will soon be able to predict lipid oxidation rates and antioxidant activity of inhibitors in colloidal systems. Given that various physicochemical processes complicate the development of the model, a combination of algorithms may be an effective solution.

This review examined the kinetics and the main stages of oxidation and inhibition of fatty acids, as well as the main research methods in oxidation kinetics. A more detailed study of the kinetics of fatty acid oxidation in colloidal solutions may predict and increase the shelf-life of various food products.

CONTRIBUTION

I.V. Moskalenko developed the research concept, conducted the research, wrote and proofread the manuscript, supervised the project, and obtained funding. I.S. Korolev contributed to the writing of the manuscript and prepared the illustrations. E.A. Smirnov contributed to the writing and proofreading. E.V. Skorb developed the research concept, provided text editing, and obtained funding.

CONFLICT OF INTEREST

The authors declared no conflict of interests regarding the publication of this article.

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