Initiation of Oxidative Processes in Muscle Foods

KENNETH W. MC MILLIN*

Introduction

The physical and chemical changes in muscle foods during the conversion of muscle to meat and post-mortem storage and utilization may alter the quality, amount, nutritional value, healthfulness and safety of meat. The quality properties are affected by biophysical interactions (Swatland, 1989) and physicochemical events (Acton et al., 1983). Changes in product or external conditions during storage result in deterioration of quality, including discoloration, development of off-flavors, loss of nutrients, textural changes and progression of spoilage and/or pathogenicity (Skibsted et al., 1994). Metabolic reactions resulting from biological membrane disruption (Stanley, 1991) and biochemical oxidative processes (Xiong and Decker, 1995) are major influences on deteriorative changes.

Muscle foods are susceptible to oxidative activity because of their lipid, protein, pigment, vitamin and carbohydrate composition (Kanner, 1994). For this review, oxidation will be defined as the transfer of electrons, hydrogen abstraction or flow of unpaired electrons. With this definition, oxidative processes may occur with all chemical constituents in muscle foods. Although it is common to refer to factors that initiate oxidative processes in foods as "catalysts," chemical catalysts are usually defined as substances that provide a low energy alternative mechanism or pathway for production of reaction products and may be recovered from the reaction mixture chemically unchanged (Brady and Humiston, 1975). Using these basic definitions of oxidative processes and catalysts, there would be few initiators of oxidation in biological materials that are chemically unchanged during the oxidation-reduction reactions.

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K.W. McMillin, Dept. of Animal Science, Louisiana State University, Agricultural Center, Baton Rouge, LA 70803-4210.

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Oxidative Processes

The biological muscle food compounds that are most influenced by oxidative processes include unsaturated fatty acids in lipids, amino acids in proteins, heme groups in pigments and the chains in vitamins with conjugated double bonds. There are many free radical forms of atomic species with one or more unpaired electrons that are involved in oxidation reactions. These include hydrogen atoms (H•), trichloromethyl (CCl_3•) from liver metabolism of CCl_4, superoxide (O_2•$^-$), hydroxyl (OH•), thiyl (RS•) with unpaired electrons residing on sulfur, peroxyl (RO_2•), alkoxyl (RO•) and oxides of nitrogen (NO•, NO_2•) (Foote, 1985; Halliwell et al., 1995; Kanner, 1994; Thomas, 1995).

When free radicals meet, the result is often a covalent bond between the unpaired electrons. Most molecules in biological systems are nonradicals, so contact with radicals may result in generation of new radicals through reactions of addition, reduction or electron donation, oxidation by electron acceptance, or oxidation by hydrogen atom transfer (Halliwell et al., 1995). The formation of reactive radicals may initiate free-radical chain reactions, such as lipid peroxidation, pigment discoloration, or interactions between lipids and heme pigments. The reactions of free radicals with specific molecules of biological origin have been described (Foote, 1985; Frankel, 1991; Kanner et al., 1987; Neta and Simic, 1985; Thomas, 1995).

There are several molecules in biological systems that are not free radicals, but will freely participate in free-radical reactions. The partially reduced or activated oxygen-containing compounds include hydrogen peroxide (H_2O_2) that participates in oxidase enzyme reactions; generation of superoxide anions (O_2•$^-$) through autoxidation of catecholamines, ascorbic acid and flavins; and development of singlet oxygen ($^1O_2$) by photosensitization of flavins and hematoporphyrins (Kanner et al., 1987). Molecular triplet oxygen (O_2) is prevented from direct addition to singlet state unsaturated fatty acid molecules by having a paramagnetic spin resonance (Asghar et al., 1988).

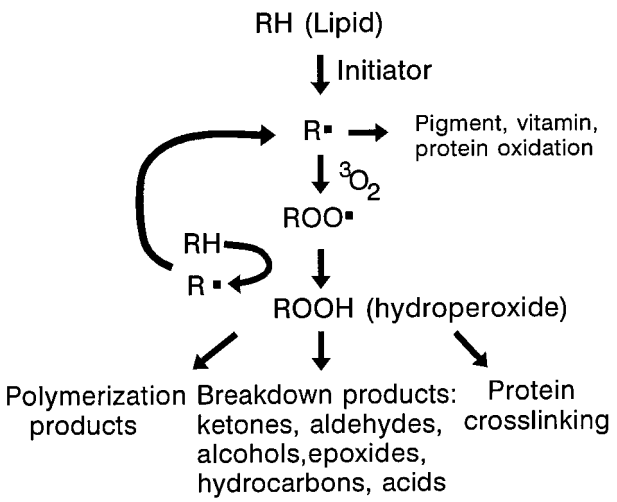
Primary activators for participation of oxygen and metal compounds in one-electron reduction processes are perhydroxyl and hydroxyl radicals, ferryl iron (IV) and lipid free radicals (Kanner, 1994). The perhydroxyl radical can penetrate membrane lipid regions and initiate lipid peroxidation (Halliwell and Gutteridge, 1986). There are several important chemical reactions between the iron in myoglobin and oxygen derivatives. These include the Fenton reaction ($Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH\bullet$), superoxide reaction ($Fe^{+3} + O_2\bullet^- \rightarrow Fe^{+2} + O_2$) and Haber-Weiss reaction ($H_2O_2 + O_2\bullet^- \rightarrow + OH^- + OH\bullet + O_2$) (Johnson et al., 1992). Martell and Khan (1973) outlined the reactions of oxygen with metal catalysts as insertion with or without cleavage of O-O bonds, non-insertion with reduction to H_2O_2 or stepwise reduction to H_2O, or disproportionation of H_2O_2.

Lipid peroxidation will occur in unsaturated fatty acids in lipid depots and in phospholipids in membranes through enzymatic and nonenzymatic autocatalytic mechanisms (Rhee, 1988; Stanley, 1991). Enzymes, including lipoxygenase, peroxidase and microsomal enzymes, which catalyze insertion of oxygen into polyunsaturated fatty acids with unconjugated dienes, have been identified in various animal tissues (Ashie et al., 1996; Hsieh and Kinsella, 1989; Kanner and Kinsella, 1983a, b; Stanley, 1991). In laboratory conditions, enzyme systems in microsomes isolated from fish sarcoplasmic reticulum vesicles produced thiobarbituric acid reactive substances (TBARS) in the presence of a reduced nucleotide (NADH or NADPH), adenosine diphosphate (ADP) and iron (McDonald et al., 1979; McDonald and Hultin, 1987). Phospholipases hydrolyze phospholipids to create conditions less favorable for chain propagation, perhaps by releasing free fatty acids from the membrane surface (Shewfelt et al., 1981).

The nonenzymic autocatalytic pathway of free-radical chain reaction for lipid peroxidation has been categorized into initiation, propagation and termination phases (Hamilton, 1989; Kanner et al., 1987; Karel, 1992; Labuza, 1971; Lillard, 1987; Love, 1987; Nawar, 1985; Porter, 1984; Shahidi, 1994a). The initiation of lipid peroxidation causes free radicals to react across double bonds of unsaturated fatty acids, forming peroxides that degenerate into hydroperoxides. The development of hydroperoxides may initiate more free radicals, which propagates further peroxide production (Figure 1; Shahidi, 1994a). Lipid oxidation is terminated when free radicals combine to give stable, nonpropagating reactions. Compounds that scavenge free radicals by electron- or hydrogen-donation are primary antioxidants, while secondary antioxidants deactivate or chelate the catalysts of oxidation (Labuza, 1971).

Many factors affect lipid peroxidation in animal tissues, including species, anatomical location, diet, environmental temperature, sex, age, phospholipid content and body composition (Gray and Pearson, 1987). Processing factors that influence rate of lipid peroxidation are composition of raw materials, time post-mortem, heating, comminution or particle size reduction and added ingredients such as salt, spices

FIGURE 1.



Flow diagram of muscle food lipid oxidation (adapted from Shahidi, 1994a).

and antioxidants (Kanner, 1994). Membranes contain greater percentages of polyunsaturated fatty acids than cytoplasmic fractions (Sweeten et al., 1990), with phosphatidyl choline and phosphatidyl ethanolamine contributing more lipid oxidation products than other membrane lipids (Pikul and Kummerow, 1990). The mechanisms and specific chemical reactions for individual fatty acids in muscle foods have been elucidated (Frankel, 1991; Kanner et al., 1987).

Metabolic processes that generate superoxide anions through oxygen reduction result in hydrogen peroxide by non-enzymatic dismutation or superoxide dismutase action. Hydrogen peroxide can oxidize myoglobin to initiate lipid peroxidation (Kanner and Harel, 1985). The primary hydroperoxide derivatives of lipid oxidation decompose to yield a complex mixture of products such as aldehydes, ketones and alcohols. The distinctive odor and flavor traits of these compounds have been characterized through objective and sensory measurements (Asghar et al., 1988; Gray and Pearson, 1994; Gray et al., 1994; Pearson et al., 1977; Shahidi, 1994b; Spanier et al., 1977; St. Angelo and Bailey, 1987). The decrease in desirable flavors during refrigerated storage of cooked meat may also be attributed to masking of or decreases in desirable flavor notes (Drumm and Spanier, 1991).

The processing of muscle through particle size reduction; exposure to oxygen, salt, sodium nitrite, unbound water, spices and other potential prooxidants; heating and smoking; freezing; and exposure to light create conditions that favor oxidative processes in muscle proteins. The possible oxidative reactions in proteins include radicalization, complex formation, polymerization, fragmentation, insolubilization and amino acid destruction (Xiong and Decker, 1995). Oxidation of proteins may alter physical traits of processed muscle foods, such as gelation, emulsification, solubility and cohesion (Xiong, 1994; Xiong and Decker, 1995). Amino acids most susceptible to oxidation are those with reactive

side chains (Feeney et al., 1985; Finley, 1985; Schaich, 1980a,b; Xiong and Decker, 1995). The major aspects of muscle food protein oxidation and influences on meat properties are discussed in these proceedings (Xiong, 1996).

Meat color is primarily influenced by the concentration and chemical state of heme pigments, myoglobin and hemoglobin and the physical meat structure, which determines incident light reflectance (Seideman et al., 1984). The amounts, chemical states and ligand binding of hemoglobin and myoglobin vary with individual animals (species, age, sex, stress), meat sources (muscle location, muscle type, muscle fiber type), availability of chemicals to bind the heme, the oxidation-reduction conditions and water-binding capacities (Kropf, 1993; Seideman et al., 1984). Hemoglobin levels depend on the completeness of bleeding during slaughter, but hemoglobin accounts for less than 20% of the total pigments. Myoglobin concentration varies with physiological and anatomical characteristics of individual muscles (Faustman and Cassens, 1990, 1991; Giddings, 1974, 1977; Livingston and Brown, 1981; Seideman et al., 1984). Bloom color and oxymyoglobin were higher in loin and lower in chuck compared with round muscles (Fellers et al., 1963).

Meat pigments in the native deoxymyoglobin state are purple but are easily converted to oxymyoglobin to produce a bright red (bloomed) color with greater than 40 torr partial pressure of oxygen (Rizvi, 1981). Oxymyoglobin pigments (ferrous iron) are oxidized to the brown metmyoglobin forms (ferric iron) within 5 days of fresh meat storage at 3.3°C (Pierson et al., 1970) as the residual reduction potential in the meat is exhausted. The depth of oxygen penetration into the interior of fresh meat from the surface is marked by a brown layer of metmyoglobin (Skibsted et al., 1994) and is influenced by the time of fabrication post-mortem, ground or intact form and time of air exposure before packaging (McMillin et al., 1994; Millar et al., 1994; O'Keeffe and Hood, 1982).

Each pigment molecule is independent of other pigment molecules and the three states of myoglobin exist simultaneously in varying amounts, interchanging among oxidative states as oxidation-reduction potentials change. The oxidation and reduction states of pigments in fresh meat have been previously reviewed (Faustman and Cassens, 1990; Giddings, 1977; Kropf, 1993; Seideman et al., 1984). The relationship of oxygen partial pressure to pigment forms would indicate that there may not be direct reversibility of oxidation-reduction potentials among the different pigment forms in uncooked meat (Hunt and Kropf, 1987; Zaritzky and Bevilacqua, 1988).

Meat color stability is highly related to inherent oxygen consumption rates, metmyoglobin reducing capacity and metmyoglobin reductase activity (Bendall and Taylor, 1972; Echevarne et al., 1990; Hood, 1980; Kropf, 1993; Lanari and Cassens, 1991; Madhavi and Carpenter, 1993; O'Keeffe and Hood, 1982; Reddy and Carpenter, 1991). Oxygen consumption by mitochondria or mitochondrial components assists in maintaining pigments in a deoxymyoglobin state (Ashmore et al., 1972; Cornforth and Egbert, 1985; Egbert and Cornforth, 1986; Giddings, 1974, 1977; Renerre and Labas, 1987). Microsomes and intact mitochondria fractions had the highest metmyoglobin reductase activity, but specific enzyme systems were not identified (Echevarne et al., 1990). The presence of metmyoglobin reductase was reported and identified as a NADH-cytochrome b_5 reductase (Arihara et al., 1989). The rate of metmyoglobin accumulation was shown to be affected by tissue oxygen consumption rate (O'Keeffe and Hood, 1982; Renerre and Labas, 1987). Lanari and Cassens (1991) found that beef muscles of lower color stability had higher oxygen consumption rates and metmyoglobin reducing abilities and the oxygen consumption rate decreased with time post-mortem.

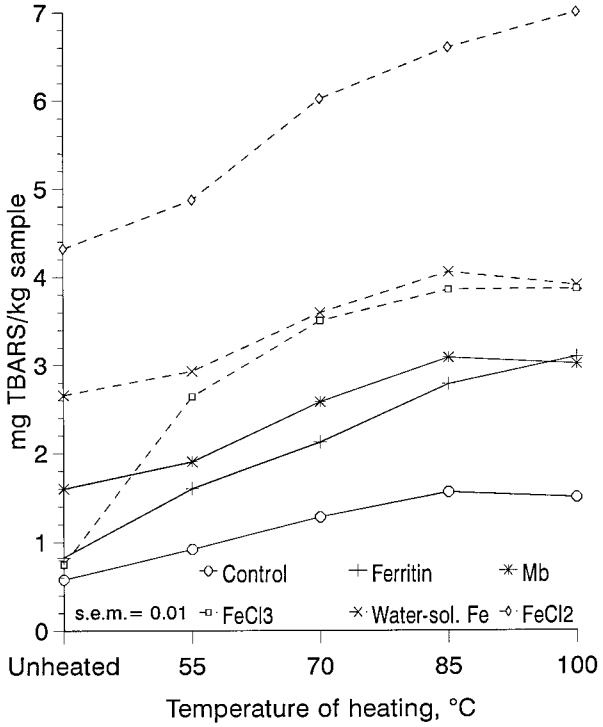
The stability and maintenance of bloomed color due to different muscle types and biochemical changes (Faustman and Cassens, 1990; Hood, 1980; O'Keeffe and Hood, 1982; Renerre and Labas, 1987) are influenced by temperature, package vapor permeability and package atmosphere composition (Kropf, 1980). Autoxidation of oxymyoglobin to metmyoglobin generates superoxide anions, which are converted immediately into H_2O_2 by spontaneous dismutation (Gotoh and Shikama, 1976). Superoxide formation was shown to be due to a nucleophilic displacement of superoxides from oxymyoglobin by water or OH• in the heme (Shikama and Matsuoka, 1986). Ferryl-myoglobin (IV) is generated by reactions of metmyoglobin with H_2O_2 (Davies, 1989; Newman et al., 1991; Kanner, 1994; Tajima and Shikama, 1987).

Muscle foods are an important source of the B-complex vitamins, including thiamin, riboflavin, niacin, biotin, patothenic acid and folacin (Briggs and Schweigert, 1990). Fat-soluble vitamins (A, D, E, K) are also involved in the metabolic reactions in muscle tissues. The stability of vitamins varies greatly with storage and processing procedures (Gregory, 1985). Vitamins, most particularly those with chains containing conjugated double bonds, participate in cellular oxidation-reduction reactions, physiologically functioning as coenzymes, central metabolites and electron-transfer agents. Oxidative changes may influence the amounts, functions and bioavailability of vitamins in meat. The many forms and changes of vitamins in foods have been summarized (Clydesdale et al., 1991; Gregory, 1985; Hawkes and Villota, 1989; Johnson, 1995; Sauberlich, 1990; Smith, 1990; Sommers and Hagen, 1980; Windham et al., 1990). The influences of vitamins on fresh meat color stability are presented in these proceedings (Faustman et al., 1996).

Initiation of Oxidative Processes in Muscle Foods

There are several inherent and exogenous initiators of oxidation in muscle foods, including heat, light, metals, pigments, freezing, water availability, salt, air (oxygen), enzymes and alkaline conditions. These will be briefly discussed in relation to conditions during processing and/or storage and display of fresh muscle foods.

FIGURE 2.



Lipid oxidation in aqueous beef residue model systems with heating and different iron forms (from Han et al., 1995).

Inherent Factors

Development of lipid oxidation caused by heating that results in the "warmed-over" flavor of cooked meat during refrigerated storage has been well documented (Asghar et al., 1988; Pearson et al., 1977; St. Angelo and Bailey, 1987). Heating is believed to release inorganic iron from muscle pigments to promote lipid oxidation (Gray et al., 1994). Denaturation by heat leads to a release of free iron (Igene et al., 1979; Morrissey and Tichivangana, 1985), which was highly correlated with lipid oxidation in poultry muscles (Kanner et al., 1988a, b). Ferritin has been identified as a main source of free iron for the lipid peroxidation (Decker and Welch, 1990; Kanner and Doll, 1991; Seman et al., 1991).

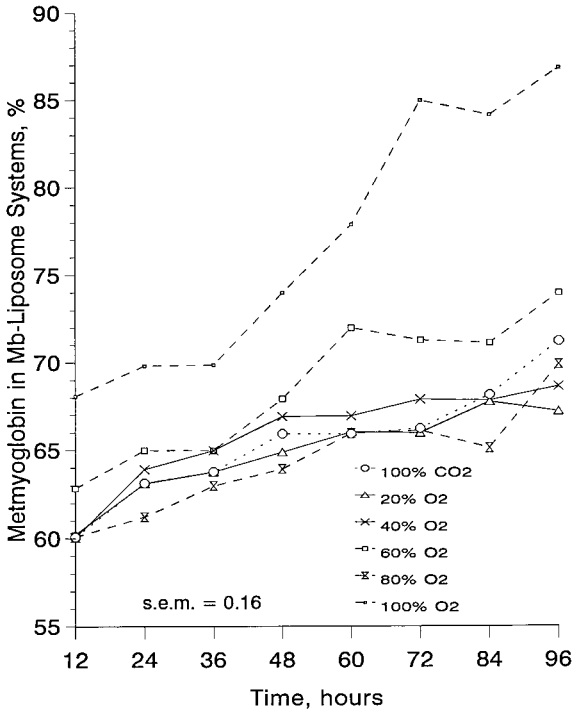
More than 75% of soluble iron is associated with the heme fraction, while the low molecular weight fraction of iron was the major catalyst for lipid oxidation at physiological concentrations (Apte and Morrissey, 1987). Han et al. (1993) quantified the distribution of different iron forms in beef and chicken muscle and found that insoluble iron concentration increased with heating. Nonheme iron was identified as a prooxidant in cooked meat, with little oxidative activity by myoglobin (Love and Pearson, 1974). In another study, heme irons had greater prooxidant effects than inorganic iron, but oxidation was not influenced by mode of prooxidant addition or the rate of cooking (Monahan et al., 1993). Lipid oxidation proceeded during heating of aqueous muscle extracts with only trace concentrations (ppm) of iron and rates of oxidation increased after exposure to water-soluble, diffusate, nondiffusate, pigments and hematin forms of iron inherent in beef muscle (Figure 2)(Han et al., 1995). Cytosolic reducing compounds seemed responsible for activation of the iron-redox cycle and for inhibiting H_2O_2-activated myoglobin from initiating membranal lipid peroxidation (Kanner et al., 1991b). Heating resulted in more nonheme iron and treatment with heat and H_2O_2 destroyed the iron-porphyrin complex in ground beef extracts. (Schricker and Miller, 1983). The contradictory results of the many studies on forms of iron in meat and meat-derived systems may be due to the presence or absence of cytosolic fractions that contain pro- and antioxidant compounds (Kanner, 1994). Catalase, which is present in uncooked meat and destroyed by heating, inactivates H_2O_2 and could provide an explanation for the more rapid development of lipid oxidation in cooked than in raw muscle foods (Harel and Kanner, 1985). The heme pigment content in conjunction with the activity of catalase may provide an indication of lipid oxidation potential in raw meat, with polyunsaturated fatty acid amounts being a major determinant of inter-species oxidation rate differences (Rhee et al., 1996).

The changes in myofibrillar proteins with heating were described by Hamm (1977) and Seideman and Durland (1984). The SH groups are oxidized to SS by oxygen as temperature increased from 70° to 120°C (Hamm and Hofmann, 1965). Myoglobin was shown to coagulate in muscle at about 65°C, lower than the denaturation temperature of the pigment in pure solution (Fogg and Harrison, 1975). Protein denaturation appeared to be mostly complete in beef steaks after heating to 80°C while visual color changes occurred at incremental temperatures between 65° and 80°C (Bowers et al., 1987). Heme degradation was less with rapid heating to denaturation temperatures compared with slow heating (Oellingrath, 1988). A pink color in cooked meat may be promoted by reducing conditions for hemochromes (Cornforth et al., 1986), which have been identified as undenatured oxymyoglobin and deoxymyoglobin pigments (Ghorpade and Cornforth, 1993).

Metals react with biological compounds through ion activation of adjacent sites on functional groups of organic compound or through electron transfer oxidation-reduction reactions with corresponding reactions in the organic compound (Martell, 1985). Metal ions will stimulate the oxidation of oxymyoglobin. Copper was more active than iron, aluminum and zinc in studies of Snyder and Skrdland (1966), while Tichivangana and Morrissey (1985) reported that iron was more highly catalytic than copper, cobalt and metmyoglobin for lipid oxidation in cooked muscle. Copper ions did not increase lipid peroxidation compared with ferric and ferrous ions in catfish muscle microsomes (Eun et al., 1993). The conflicting results may be attributable to types of phospholipids in the extract preparations, presence of other compounds or other differences in experimental conditions.

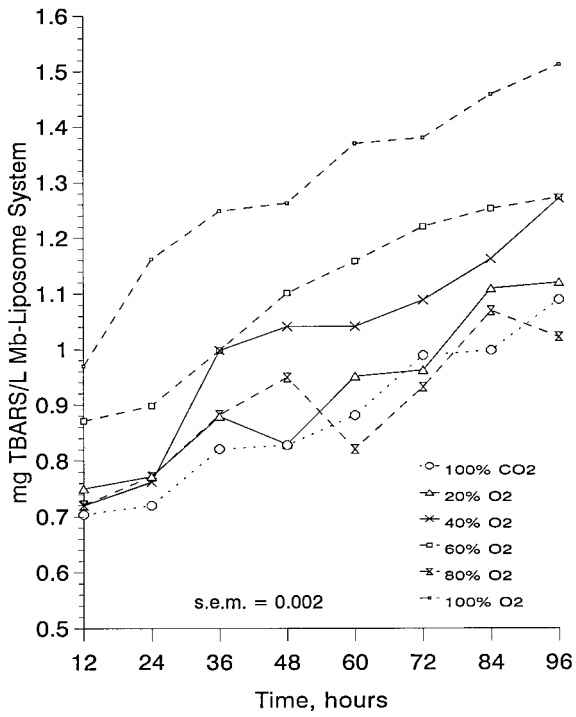
Exposure to iron and copper increased carbonyl content of proteins, indicating oxidative changes in amino acid

FIGURE 3.



Metmyoglobin formation in myoglobin-liposome systems with oxygen (from Huang, 1995).

FIGURE 4.



Lipid oxidation in myoglobin-liposome systems with oxygen (from Huang, 1995; Huang et al., 1995).

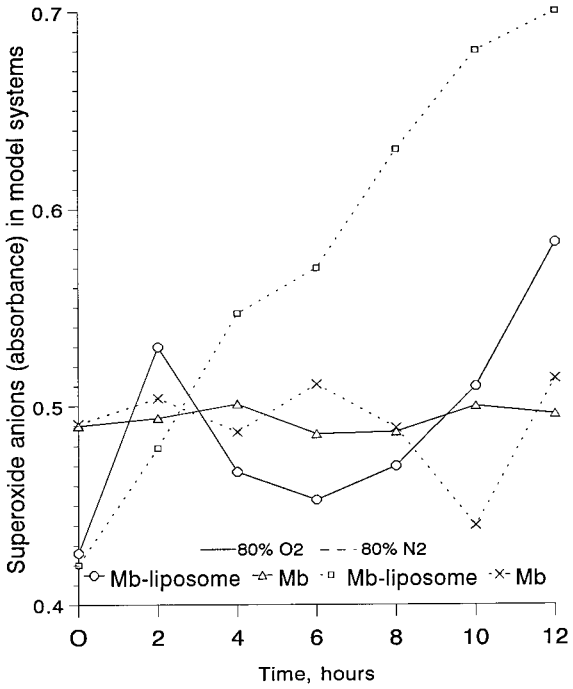
residues (Decker et al., 1993; Levine et al., 1990). Copper is rarely in sufficient amounts *in vivo* to initiate free radical reactions but is usually bound to proteins or small molecules (Johnson et al., 1992). Kanner et al. (1988b) found that muscle lipid peroxidation was dependent upon oxygen and free metal ions. The oxidation of ferric ions to ferrous ions produces superoxide, hydrogen peroxide and hydroxyl radicals (Kanner, 1994). Most of the peroxidation in minced turkey muscle was catalyzed by free iron ions (Kanner et al., 1988a). Collagen was oxidatively degraded by metal-catalyzed free radical systems with copper and iron combined with ascorbate or H_2O_2 to cause loss of proline and depolymerization of protein (Uchida et al., 1992).

Oxygen is a determinant of oxymyoglobin, with a minimum of 40 mm Hg oxygen pressure required to maintain oxymyoglobin (Rizvi, 1981). Metmyoglobin formation was reported to be maximum at 6 mm Hg O_2 at 0°C (Ledward, 1970). While some studies have shown more surface discoloration with high O_2 (Seideman et al., 1979), there are also reports that meat in 80% to 100% O_2 developed less metmyoglobin or had more desirable color than samples in anoxic or air environments (Daun et al., 1971; Hermansen, 1983; Huffman et al., 1975). Figures 3 and 4 show that metmyoglobin formation and lipid oxidation are not directly influenced by oxygen concentration in myoglobin-liposome solutions (Huang, 1995; Huang et al., 1995).

Under air-saturated conditions, H_2O_2 was decomposed by metmyoglobin, while at lower O_2, H_2O_2 was a potent oxidant of deoxymyoglobin (Tajima and Shikama, 1987; Wazawa et al., 1992). The consumption of O_2 by mitochondrial components is believed to maintain myoglobin in a reduced state (Cornforth and Egbert, 1985, Renerre and Labas, 1987). O_2 is unlikely to directly cause development of free radicals because it is in the triplet state, the most stable form (Rawls and Santen, 1970). Singlet oxygen, generated by photooxidation of O_2 by light and sensitizers from chemical, enzymatic, gaseous or hydroperoxide decomposition sources, is a more potent initiator of oxidative processes than O_2 (Bradley and Min, 1992). A triplet-excited sensitizer molecule may directly interact with another molecule to generate free radicals (Type I pathway) or transfer energy to atmospheric O_2 to produce singlet oxygen (Type II pathway). Singlet oxygen naturally decays to triplet-state O_2, is destroyed by a quencher agent, or reacts with other singlet-state molecules to produce undesirable oxidation compounds (Bradley and Min, 1992). The porphyrin ring of myoglobin has been shown to be an effective sensitizer for singlet oxygen production (Kanner, 1992; Whang and Peng, 1988a). Koelsch et al. (1991) proposed kinetic models to quantify hexanal from lipid oxidation with increased oxygen concentrations.

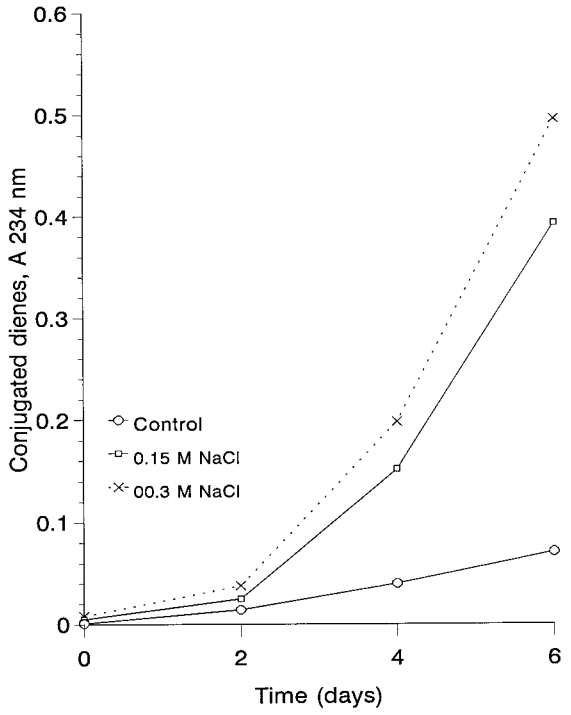
Differences in pH influence autoxidation of myoglobin, resulting in increased metmyoglobin with decreased pH (Chow et al., 1987; Chow, 1991; Shikama and Matsuoka, 1986; Yin and Faustman, 1993). At lower pH, denaturation of the globin tertiary structure would expose the heme pro-

FIGURE 5.



Generation of superoxide anion radicals in myoglobin and myoglobin-liposome systems with oxygen or nitrogen atmospheres (from Huang, 1995; Huang et al., 1996).

FIGURE 6.



Lipid peroxidation in minced dark turkey muscles with sodium chloride at 4°C (from Kanner et al., 1991a).

tein to external environments, accelerating the protonation of bound O_2 and favoring the release of superoxide anions (Fronticelli and Bucci, 1963; Livingston and Brown, 1981). A lower pH depletes NADH and activates oxygen more rapidly, resulting in increased metmyoglobin from generation of superoxide and H_2O_2 (Skibsted et al., 1994). More free iron and lipid oxidation were observed in post-rigor ground pork muscles than in pre-rigor ground pork (Tay et al., 1983). Higher pH levels, due to hot processing, decreased lipid oxidation in ground pork (Judge and Aberle, 1980; Yasosky et al., 1984) and increased color and lipid stability in frozen minced beef compared with post-rigor beef (Andersen et al., 1990). Myoglobin from different seafood species had minimal oxidation with increased pH, which was associated with higher myoglobin stability (Chow, 1991). Pre-rigor cooked roasts had equivalent or improved oxidative stability compared with post-rigor cooked roasts and beef roasts had relatively low lipid oxidation during storage while pork roasts had high lipid oxidation (Shin et al., 1993). Color stability of hot-boned cow muscles was only slightly more stable in retail display than cold-boned muscles (Van Laack et al., 1989).

Lipid peroxidation and myoglobin pigment oxidation appear linked in refrigerated uncured meat (Kanner et al., 1987). Lin and Hultin (1977) found increased oxidation of oxymyoglobin upon incubation with enzymic lipid peroxides of a chicken muscle microsome fraction. The superoxide anions generated during lipid oxidation are converted immediately and almost completely into hydrogen peroxide (Gotoh and Shikama, 1976). The reaction of metmyoglobin with hydroperoxide species may generate peroxyl radicals involved with the intact heme moiety to produce a protein-derived radical (Davies, 1989). Hydrogen peroxide and hydroxy radicals are potent prooxidants of phospholipids (Tajima and Shikama, 1987). The generation of superoxide anions in liposome-myoglobin systems corresponded with a decrease in oxymyoglobin and the oxidation of pigments and lipids increased in the presence of both myoglobin and liposomes (Figure 5)(Huang, 1995; Huang et al., 1995). Johns et al. (1989) stated that H_2O_2 formed by autoxidation of oxypigments might be necessary for ferric heme pigments to initiate lipid oxidation.

Heme-containing pigments have been strongly implicated as initiators of lipid oxidation, particularly during heating or during refrigerated storage of muscle foods after heating (Govindarajan et al., 1977; Greene, 1969; Rhee et al., 1986; Rhee and Ziprin, 1987). Autoxidation of oxymyoglobin results in metmyoglobin and superoxide radicals, which dismutate to H_2O_2 (Brown and Mebine, 1969; Misra and Fridovich, 1972; Gotoh and Shikama, 1976). The interaction of H_2O_2 with metmyoglobin caused activation of metmyoglobin that resulted in oxidative initiation (Kanner and Harel, 1985; Rhee, 1988) by production of free radicals (King and Winfield, 1963). Conversely, malondialdehyde from degradation of oxidized polyunsaturated fatty acids has been shown to induce protein to protein cross-links in myosin through Schiff's base reactions (Buttkus, 1967).

Exogenous Factors

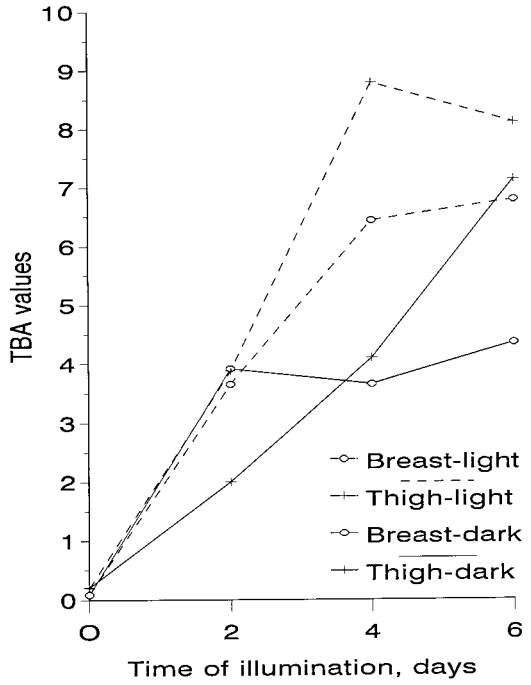
Sodium chloride (salt) has been suggested as a prooxidant for lipids (Pearson et al., 1977). Pre-rigor grinding and salting of ground beef reduced extent of metmyoglobin formation, while salt accelerated lipid oxidation during storage at 4°C in both pre-rigor and post-rigor beef (Torres et al, 1988). Salt in restructured beef steaks increased lipid oxidation during frozen storage, but there were no differences between NaCl or KCl with use of antioxidants (Wheeler et al., 1990). This contrasted with reports that NaCl resulted in more rancidity than KCl in restructured beef steaks (Miller et al., 1986) and in turkey patties (King and Earl, 1988). Use of phosphates inhibited some lipid oxidation but did not prevent discoloration in frozen restructured beef, pork and turkey containing salt (Akamittath et al., 1990). Increased pH decreased the rate of metmyoglobin formation in beef, turkey and pork containing salt (Trout, 1990).

Asghar et al. (1990) suggested that suppression of microbial growth might be the mechanism by which salt stabilizes color in pre-rigor minced meat rather than by enzymes of subcellular organelles. Compared with pigment oxidation, lipid oxidation showed an initial lag in frozen pork patties containing salt, while a UV-light absorber inhibited light-dependent lipid oxidation but only partially prevented discoloration (Andersen and Skibsted, 1991). Higher salt increased accumulation of lipid peroxidation products (Figure 6), but decreased lipid peroxidation in the presence of ascorbic acid and iron in a model washed-muscle residue system (Kanner et al., 1991a). NaCl enhanced the activity of iron ions, which was partly attributed to the ability of NaCl to displace iron from binding macromolecules (Kanner, 1994). Use of collagen in ground beef that contained salt did not influence lipid oxidation (Farouk et al., 1991). The activity of copper as a pro-oxidant increased with the presence of salt in pork phospholipid liposomes at freezing temperatures (Arnold et al., 1991).

Curing reactions will influence oxidative processes in muscle foods. The use of nitrates and nitrites, formation of nitroso compounds and interactions with other added ingredients such as salt, phosphates and reducing agents are too complex for discussion in this paper, even though nitrites are highly reactive ions (Townsend and Olson, 1987). A complete history of reactions and controversies on use of nitrites for curing (Cassens, 1990), overviews of nitrite use and nitroso compounds in foods (IFT, 1987; Sebranek, 1979) and the role of nitrite in cured meat flavor (Gray et al., 1981) are available.

Exposure to light will also accelerate lipid peroxidation in muscle foods (Whang and Peng, 1988a, b; Zachariah and Satterlee, 1973; Solberg and Franke, 1971). White fluorescent lighting was more destructive of surface oxymyoglobin than incandescent lighting (Satterlee and Hansmeyer, 1974) and freezing temperatures accelerated the autoxidation of oxymyoglobin (Zachariah and Satterlee, 1973). More oxymyoglobin was converted to metmyoglobin with ultraviolet than visible light (Bertelsen and Skibsted, 1987). Setser et al. (1973) reported a protective effect of oxygen on oxymyoglobin maintenance under lighting. A review of retail display conditions on meat color provided indications that some lighting sources improved color emission balance, greater lighting intensity increased pigment oxidation and higher temperatures increased oxymyoglobin autoxidation rates (Kropf, 1980). Singlet oxygen was implicated as being induced by illumination to initiate lipid oxidation in ground turkey and pork (Figure 7)(Whang and Peng, 1988b). Metmyoglobin in frozen meat blocks increased with increased oxygen permeability of packaging and light in conjunction with oxygen increased both lipid and pigment oxidation compared with only light exposure (Brewer and Wu, 1993).

FIGURE 7.



Lipid oxidation in ground turkey breast and thigh meat at 4° C in dark or illuminated with 350 ft-candles (from Whang and Peng, 1988b).

Frozen storage may cause protein denaturation, recrystallization, lipid oxidation and sublimation (Calvelo, 1981). Quick freezing and thawing did not result in much denaturation of muscle protein, while slow freezing destroyed protein structure due to large ice crystal formation between cells (Deatherage and Hamm, 1960). This was confirmed by Ledward and Macfarlane (1971), although oxidation of meat lipids during freezing and frozen storage had been previously reported (Awad et al., 1968; Keller and Kinsella, 1973). Color of frozen meat was dependent upon rate of freezing and was stable if stored at low temperatures in dark conditions (Kropf, 1971). Sarcoplasmic protein solubility decreased only after long storage (Khan et al., 1963). Blast freezing resulted in more lipid oxidation in beef patties than cryogenic methods (Sebranek et al., 1979). Wanous et al. (1989)

reported that internal color of pork sausage was improved after three weeks of frozen storage, metmyoglobin increased after four weeks and sausage with the fastest freezing rate had lower color values. Frozen and thawed pork chops had more soluble protein and darker color than fresh pork (Greer and Murray, 1991). The color of minced beef decreased during frozen storage, with 1% sodium chloride causing more severe discoloration than exposure to light (Andersen et al., 1990).

Other factors influencing meat pigment and lipid stability include microbiological factors, temperature, air velocity and relative humidity (Faustman and Cassens, 1990). Bacterial growth will greatly increase the rate of discoloration, primarily by reduction of O_2 tension on the meat surface (Robach and Costilow, 1961), although Lin et al. (1977) found that *Pseudomonad* microorganisms did not increase myoglobin oxidation. *Enterococci* species converted metmyoglobin to oxymyoglobin (Ariharia et al., 1994). Metmyoglobin formation is prompted by increased temperatures, greater air velocity and higher relative humidity (Lanier et al., 1977). The discoloration of prepackaged meat at 10°C was two to five times greater than at 0°C, with variations among muscles (Hood, 1980). Measurements of oxygen uptake indicated that lipid oxidation increased with higher temperatures and higher water activity, although results were influenced by differences in initial oxygen content because oxygen solubility is higher at lower temperatures and higher water content (Prado and Taylor, 1995). A sufficient reduction in O_2 tension resulted in little or no formation of H_2O_2, resulting in greater stability of pigments (Reddy and Carpenter, 1991; Arihara et al., 1993). Subjection of water to high energy ionization produces hydroxyl radicals while singlet oxygen can be developed through photochemical reactions (Foote and Wexler, 1964). Increasing temperatures, air velocity and relative humidity promoted metmyoglobin formation (Lanier et al., 1977).

Conclusions

Oxidation through electron transfer, hydrogen abstraction, or exchange of free electrons may alter many of the chemical compounds in muscle foods. Unsaturated fatty acids in lipids, amino acids in proteins, heme groups in pigments and conjugated double bonds in vitamins are influenced by oxidative reactions with free radicals, enzymes and oxygen derivatives. Inherent muscle properties, storage and processing to cause pigment or lipid degradation, metal ions, pH, enzymes, salts, heating, freezing, light exposure and exposure to air or oxygen may initiate oxidative processes in muscle foods. More information on the basic metabolic changes in meat products would provide insight on inhibition of oxidation and stabilization of muscle food quality.

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