Metal Ion Catalysis of Autoxidation in a Lard Gel[1]

R. ELLIS, G.T. CURRIE and A.M. GADDIS, Meat Laboratory,[2] Beltsville, Maryland 20705

Abstract

The prooxidant effects of transition metal compounds upon lard triglycerides in an aqueous heterogeneous model system were examined. Catalytic activity of a metal salt depended on its identity, the phase in which it is dissolved, the buffering salts and pH of the system. The iron and copper inorganic salts dissolved in the aqueous phase were powerful catalysts. Other transition metal salts had little positive effect on autoxidation at acid and neutral pH values. Manganous chloride had an inhibiting action. Freeze-drying reversed catalysis patterns, and Mn^{++} and Co^{++} became the strongest prooxidants. Cobaltous and manganese stearates were the most active of such compounds. Reversals in catalytic activity were due to the formation or disappearance of aquo ions.

Introduction

This research was initiated because of the need for a more complete knowledge of the factors which influence the autoxidation of lipids in meat and meat products. An earlier study (1) demonstrated that only tentative conclusions could be reached in the study of mechanisms of the prooxidant action of sodium chloride on the triglycerides of frozen meat. Use of some type of model system was considered applicable to the necessity for simplification. A suitable model system should permit selection of factors and variations in environmental conditions related to the processing and storage of meat.

A gel composed of lard, water, sodium carboxymethyl cellulose (CMC) and appropriate additives was determined to fulfill most of the requirements needed for the type of system needed (2). This system should enable isolation of prooxidant and inhibitory factors and permit their evaluation. The model system appeared adaptable to different conditions of storage and physical states, e.g., at 20 C as a hydrated gel, frozen storage and freeze-dried.

In studies of the mechanisms of lipid autoxidation in meat, the influence of metals under heterogeneous conditions is a subject of first consideration. Much progress has been made in research on metal catalysis (3–5). However, most of this work has been done in organic solvents under conditions not remotely resembling a meat system, or a heterogeneous mixture of polar and nonpolar phases. Due to the great variety of substrates used, many of the results are conflicting in nature. Investigations by medical researchers (6) working with cells and cell walls have indicated that trace metals such as iron and copper may have as great an influence on lipid oxidation processes as the heme pigments. A study of the effect of trace amounts of transition metal compounds was made on the lard gel systems.

Experimental Procedures

Materials and procedures were the same as those described in earlier publications (1,2), except as specifically noted in Results and Discussion. Based on the gel composition of 1:2:40 by weight of sodium CMC, lard and water, additives were 1.5×10^{-4} molar in concentration or 6.45×10^{-5} moles/20 g lard in the gel, or fractions or multiples thereof as particularly stated and defined.

Results and Discussion

Effect of pH and Buffer

Most of the research on heterogeneous lipid systems has been with linoleic acid or esters or aqueous fat emulsions. Research by Spetsig (7), Saunders et al. (8), Mabrouk and Dugan (9) and Wills (6) has indicated strong influences in most cases by pH and buffers on autoxidation and its catalysts. It was therefore necessary to determine the behavior of the gels with respect to these.

Phosphate (0.10–0.01 M) buffered gels were considerably influenced by pH values. As shown in Figure 1, peroxide values decreased from pH 4.2 to

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[2] E. Market. Nutr. Res. Div., ARS, USDA.

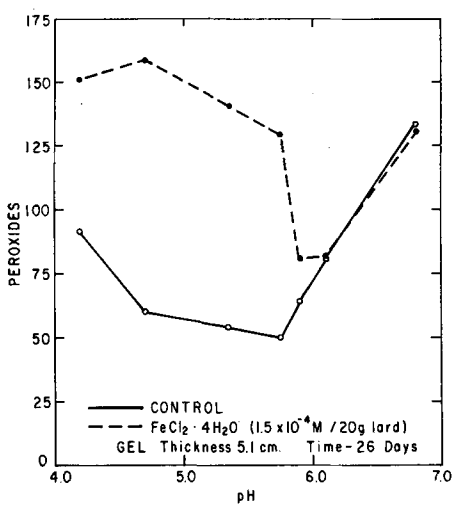

FIG. 1. Effect of phosphate buffered pH on oxidation of lard gel at 20 C.

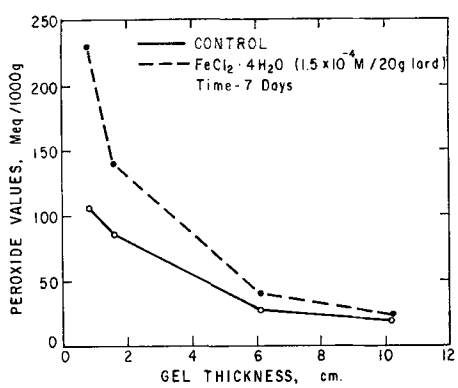

FIG. 2. Effect of gel thickness on oxidation of lard gel at 20 C.

TABLE I

Example of the Failure of Peroxide Values to Indicate Differences in Hydrated Gels Oxidized 21 Days at 20 C[a]

	Peroxides[b]	Monocarbonyls[c]
Control	65.0	0.520
Control + $FeCl_2$	65.0	1.350
Control + $FeCl_2$ EDTA	64.0	1.000
Control + $FeCl_2$, O-phenanthroline	69.0	3.400

[a] All additives 1.5 × 10^{-4} molar pH 5.4, no buffer, 10.2 cm gel thickness.
[b] Eq/1000 g lard.
[c] Absorbance in 100 ml CCl_4 of monocarbonyl 2,4-dinitrophenylhydrazones from 10 g lard.

TABLE II

Effect of Increasing Amount of Metal Salts 14.3 Times[a]

5.1 cm gel thickness	Peroxide values[b] 1[c]	6	9	14
PO_4 buffer pH 5.6				
Control	0.0	8.0	15.0	33.0
$FeCl_2 \cdot 4H_2O$	2.3	84.0	145.0	.....
$CoCl_2 \cdot 6H_2O$	0.0	8.5	17.0	38.0
$MnCl_2 \cdot 6H_2O$	....	0.0	0.0	4.0
PO_4 buffer pH 6.8				
Control	....	14.0	39.0	110.0
$FeCl_2 \cdot 4H_2O$	2.6	50.0	100.0	194.0
$CoCl_2 \cdot 6H_2O$	0.0	32.0	54.0	126.0
$MnCl_2 \cdot 6H_2O$	0.0	0.0	0.0	16.0

[a] Metal salts 2.15 × 10^{-3} molar.
[b] Eq/1000 g lard.
[c] Number of days.

4.7 and leveled from pH 4.7 to 5.7. The rate of autoxidation increased abruptly from pH 5.7 to 6.7 to a maximum at the highest pH. Mabrouk and Dugan (9), using phosphate buffers in methyl linoleate emulsions, observed an increase in rate of autoxidation as pH increased. Wills (6) studied oxidation of linoleic and linolenic acid emulsions in phosphate-buffered solutions containing 10% ethanol at pH range 4.5 to 7.5. In this case, oxidation of linoleate was unaffected by pH over the range of 5.0 to 8.0 (6). Wills (6), however, observed that pH had a marked effect on metal-catalyzed oxidations. Saunders et al. (8) concluded that phosphate buffer was not suitable because it suppressed the catalytic activity of histidine. As shown in Figure 1, the activity of ferrous ion was severely depressed at about pH 6.1 in the presence of phosphate buffer. Wills (6) reported a 50% decrease in oxidation by 0.1 M phosphate with respect to control and catalysis by Fe^{+++}, ascorbic acid and hemoglobin. The function or role of phosphate in depressing oxidation is not clear. Phosphates are capable of binding metal ions, and also may form complexes with hydroperoxides. Possibly iron ions are less available (insoluble hydroxide) at the higher pH levels. However, Saunders et al. (8), using an acetate buffer, considered the optimum pH to be 6.5 for study of Fe^{++} and histidine catalysis.

Unbuffered gels, in which the pH was adjusted with mineral acid (HCl), and lactic acid buffered gels were examined. There was little difference between the two gels; this showed a tendency to increase in the rate of oxidation as pH values rose from 5.0. Gross catalysis by Fe^{++} in the unbuffered gels or lactic acid buffered gels was little changed by pH. The abrupt decrease at pH 6.0 observed in phosphate buffered gels did not take place. The general level of oxidation of lactic acid gels was somewhat lower than the unbuffered gels. The rate of oxidation of phosphate buffered gels was appreciably lower than the lactic acid gels. In controlled experiments, Fe^{++} was repeatedly shown to have little catalytic activity at pH 6.7.

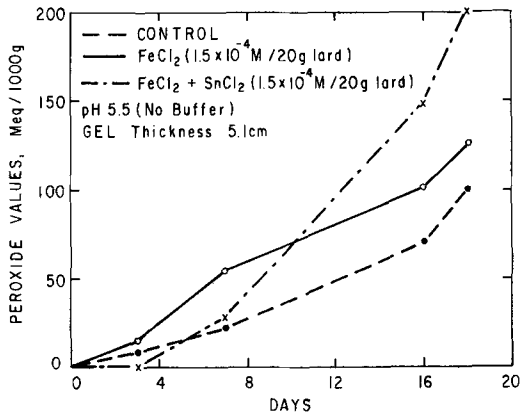

FIG. 3. Effect of $SnCl_2$ on the prooxidant action of $FeCl_2$ in a gel stored at 20 C.

TABLE III

Effect of Inorganic Metal Salts on Oxidation of Freeze-Dried Gels at 20 C[a]

	Peroxide values[b] 2[c]	3	6	13
Control	0	0	0	8.6
$MnCl_2$	384	440	532	568
$CoCl_2$	282	380	480	505
$FeCl_2$	190	252	409	400
$CuCl_2$	14	27	138	309
$NiCl_2$	0	0	0	16.0

[a] Metal salts 6.45 × 10^{-5} moles/20 g lard; no buffer.
[b] Eq/1000 g lard.
[c] Days stored.

TABLE IV

Freezer Storage at 24 F of Hydrated Gels[a]

	Peroxide values[b] (months) 2	4	7	9
Control	0.0	7.0	7.0	25.0
$FeCl_2$	6.2	24.0	164.0	180.0
$CuCl_2$	8.3	10.7	44.0	85.0
$CoCl_2$	0.0	0.0	12.0	60.0
$MnCl_2$	0.0	8.3	0.0	0.0

[a] Metal salts 6.45 × 10^{-3} moles/20 g lard; pH 5.5, no buffer.
[b] Eq/1000 g lard.

The performance of the CMC gels seemed to parallel, in most respects, results reported for lipid emulsions (6,8,9). However, the observations of Spetsig (7) differed from the above findings and reports. He observed no effect of pH 6.0 to 9.2 on the oxidation of lipid emulsions. It is of interest, however, that Spetsig (7) noted that antioxidants were rendered progressively less efficient as the pH increased from 6.0 to 6.7. Since the mildly rendered lard employed in this report contained its native tocopherol content, the antioxidant could have some bearing on the results.

The possibility that CMC could be interacting in some manner was investigated. However, there was no evidence of a serious interference. Tests with systems of wet celite, lard and 0.1% CMC suggested a small oxidation-depressing influence by the cellulose. However, this did not influence comparisons.

Phosphate or citric acid buffers had little effect on the relative activities of the various metal additives examined. However, many of the experiments were conducted without benefit of buffer at an adjusted pH of approximately 5.5, which is characteristic of meat.

Effect of Gel Thickness and Surface Areas

In meat cuts, autoxidation is almost exclusively a surface phenomenon. Desiccation or freezer burn may permit greater penetration of air on the surface but

TABLE V

Catalytic Effect of Metal Stearates[a]

	Peroxide values[b] (days)		
	8	14	21
Control	36.0	66.0	143
$FeCl_2$	65.0	116.0	250
Fe^{++} stearate	60.0	83.0	190
Cu^{++} stearate	63.0	96.0	160
Ni^{++} stearate	46.0	66.0	141
Co^{++} stearate	102.0	150.0	242

[a] Metals 1.5 × 10^{-4} molar; pH 5.5, no buffer; 5.1 cm gel thickness.
[b] Eq/1000 g lard.

TABLE VI

Monocarbonyl Compounds Developed by Aquated Metal Ions[a]

	Six days			Eight days		
	Peroxide value[b]	Monocarbonyl[c]	Ratio C=O/PV[d]	Peroxide value[b]	Monocarbonyl[c]	Ratio C=O/PV[d]
Control	73.0	0.400	0.0055	116	0.565	0.0049
$FeCl_2$	108.0	0.750	0.0069	160	1.370	0.0086
$CuCl_2$	86.0	0.503	0.0058	124	0.435	0.0035
$CoCl_2$	78.0	0.445	0.0057	116	0.570	0.0049
$MnCl_2$	69.0	0.397	0.0058	106	0.260	0.0024

[a] Metal salts 1.5 × 10^{-4} molar; pH 5.5 adj., no buffer; 1.5 cm gel thickness.
[b] Eq/1000 g lard.
[c] Absorbance in 100 ml CCl_4 of monocarbonyl 2,4-dinitrophenylhydrazones from 10 g lard.
[d] Carbonyl-peroxide ratio with oxidation.

this still amounts to a superficial effect. The interior of meat is also defended by enzyme systems which maintain a reducing medium.

A pitfall exists in application of lard-CMC gels due to exhaustion of the internal content of oxygen. Considerable incorporation of oxygen apparently takes place during the blending as shown by the relatively rapid onset of oxidation achieved. However, this internal oxygen seems to be rapidly dissipated. The effect of gel thickness on rates of oxidation in an unbuffered gel at pH 5.5 is displayed in Figure 2. As gel thickness decreased with resultant greater surface area, the overall rate of oxidation rapidly increased. In the case of thick gels, the influence of additives on oxidation may be masked so far as peroxide values are concerned. This is shown in Figure 2, which indicates very small differences in peroxide values between ferrous ion catalysis and the control in the thicker gels. During fat oxidation, peroxide formation is accompanied by peroxide decomposition. In the case of oxygen insufficiency, reactions occurring internally differ from those at the surface and may predominate. In a thick gel, the effect of ferrous ion catalysis on the peroxide decomposition reaction may be emphasized and, as shown in Table I, result in much higher monocarbonyl compound values per unit of peroxide.

Effect of Inorganic Metal Salts on Hydrated Gels

Studies of the activity of various inorganic metal salts in the promotion of oxidation of lard gels at 20 C emphasized the relatively high activity of iron ions. At the concentration of 6.45 × 10^{-5} moles/20 g lard (8 ppm in gel) and pH 5.5 (buffered or unbuffered) the order of activity was $Fe^{++} > Fe^{+++} > Cu^{+} > Cu^{++} > Ni^{++} > Co^{++}$ = Control > $Mn^{++} > Sn^{++}$. Ferric ion was slower acting than the ferrous ion. This effect of the lower valence ion has been explained by Ingold (11) on the basis of differences in rate of hydroperoxide decomposition. Iron and copper were practically the only metallic ions with catalytic activity; nickel had little effect and cobaltous ion showed little or no activity. Manganous ion inhibited oxidation strongly. The apparently

TABLE VII

Effect of Stearates on Monocarbonyl Formation[a]

	Four days			Six days		
	Peroxide value[b]	Monocarbonyl[c]	Ratio C=O/PV[d]	Peroxide value[b]	Monocarbonyl[c]	Ratio C=O/PV[d]
Control	33.0	0.360	0.011	91.0	0.523	0.0057
Ferrous stearate	68.0	0.510	0.0075	144.0	0.850	0.0059
Cupric stearate	64.0	0.565	0.0088	123.0	0.680	0.0052
Cobaltous stearate	132.0	1.270	0.0096	270.0	2.150	0.0079
Manganous stearate	67.0	0.345	0.0051	160.0	0.668	0.0042

[a] Metal salts 1.5 × 10^{-4} molar; pH 5.5, no buffer; 1.5 cm gel thickness.
[b] Eq/1000 g lard.
[c] Absorbance in 100 ml CCl_4 of monocarbonyl 2,4-dinitrophenylhydrazones from 10 g lard.
[d] Carbonyl-peroxide ratio with oxidation.

inert behavior of Co^{++} and the inhibitory activity of Mn^{++} under aqueous conditions are not entirely surprising when reports in the literature are considered in proper context. The environment and nature of the metallic compound influence catalytic properties. Generally metal ions are more readily oxidized in nonpolar or organic media. It has been pointed out by Ingold (4) that in both polar and nonpolar systems, catalysis of autoxidation does not commence until the catalyst appears in its higher valency state. Apparently Co^{++} and Mn^{++} ions cannot be oxidized to the higher valence in acidic and neutral aqueous media, whereas the cycle readily takes place in the case of Fe^{++} and Cu^{++} ions. Copper probably represents something of the other extreme, in which the Cu^{+} ion tends to bbe unstable. The effect of aqueous conditions is directly due to the formation of metal ion complexes with water. Uri and coworkers (5) have shown that, under aqueous conditions, Co^{++} and Mn^{++} ions have no catalytic efficiency as reduction activators of hydrogen peroxide, and also resist reaction with oxygen. Ferrous and Cu^{++} ions under these conditions showed favorable thermodymanic properties (5).

The work of Wills (6) in an aqueous medium containing 10% ethanol indicates the unpredictability of metal catalysis. In emulsions of linoleic and linolenic acids of pH 6.0 to 7.0 and metal concentrations of 3.3 × 10^{-3} molar or less, metal catalysis rate of oxidation rankings were $Co^{++} > Mn^{++} > Cu^{++} > Fe^{++} > Fe^{+++}$. Co^{++} had a very high rate of oxidation under these "aqueous" conditions. In contrast, in the aqueous gels, Co^{++} was ineffective catalytically from unbuffered pH 5.0 to pH 6.9. An explanation of this reversal would appear to be among the following. The ethanol prevented formation of aquated ions. Metal soaps of the unsaturated fatty acid were formed, thereby creating a more nonpolar situation.

Manganous and Co^{++} ions have similar energetic characteristics (5) but their action was considerably different in the aqueous gels. Cobaltous ion seemed virtually inert, but Mn^{++} showed strong inhibitory characteristics and produced a long induction period. Ingold (11) has reported that Mn^{++} produces an induction period which lasts until all of it is converted to the Mn^{+++} state. However, these experiments were not directly comparable to the gels since metal decanoates were used under nonpolar conditions. It is possible that Mn^{++} in the gels may react with hydroperoxides in a terminating way as suggested by Gol'dberg and Obukhova (12).

Ingold (11) has pointed out that metals may function as catalysts below a critical concentration and in-

hibitors above it. In the hydrated gels where the metals were present as aquated ions there was no evidence of a critical concentration at the molarities of 1.5×10^{-4} and 2.15×10^{-3} used. The effect of the latter concentration on the autoxidation catalyzed by the three metals of special interest is shown in Table II. Data are given at phosphate-buffered pH levels of 5.6 and 6.8. Ferrous ion at this higher concentration was more effective at the greater pH than the lower concentration (Fig. 1). As indicated in Table II, cobaltous ion was more active at pH 6.8. Manganous ion had a long induction period and seemed unaffected by pH level.

The previously referred to antioxidant influence of Mn^{++} ion was increased by phosphate buffer. However, this might be of little significance since phosphate has an overall inhibitory effect. In general, increase of pH toward the neutral range decreased net catalysis by the active metals. In the case of Mn^{++} and Co^{++}, there was a small decrease in their negative action as neutrality was approached. It is well known that Mn^{++} can be oxidized to the Mn^{+++} form in the basic media. Trivalent cobalt, which cannot exist in acid solutions, is also more stable in a basic environment. In these experiments, Mn^{++} had a strong inhibitory effect, while Co^{++} was nearly inert. On this basis, it might be considered that Mn^{++} is more resistant to oxidation than Co^{++}. This is hardly the case, since the potential for $Mn(H_2O)_6^{++} \rightleftarrows Mn(H_2O)_6^{+++}$ is -1.5 V, while the potential for $Co(H_2O)_6^{++} \rightleftarrows Co(H_2O)_6^{+++}$ is -1.8 V (13). The inhibitory properties of Mn^{++} must be due to some other function.

Manganous and stannous ions which were strongly inhibitory merit further comment. Stannous ions retarded oxidation when at trace concentrations. However, as shown in Figure 3, Sn^{++} ion, when combined with the Fe^{++} ion in equivalent quantities, conferred only a short-lived period of immunity. At the end of the short induction period, rate of oxidation was much more rapid than the Fe^{++} catalysis alone. It is probable that the Sn^{++} had the same effect as other reducing agents, such as ascorbic acid, and accelerated the $Fe^{++} \rightleftarrows Fe^{+++}$ cycle. Manganous ion in equivalent amounts had a somewhat similar but weaker effect. It does not seem likely that the mechanism with Mn^{++} is the same as the Sn^{++} ion. Cobaltous ion, when similarly added to a Fe^{++} catalyzed system, had no effect.

Catalytic Effect of Inorganic Metal Salts in Freeze-Dried Gels

Gels were freeze-dried to constant weight at room temperature as previously described (2). The gels that contained no additives had long induction periods when stored at 20 C in the prevailing atmosphere. Addition of inorganic metal salts before freeze-drying produced a very rapid rate of autoxidation. The order of activity of the various metal salts showed almost a complete reversal from the performance under hydrated conditions. Relative activity was $Mn^{++} > Co^{++} > Fe^{++} > Cu^{++} > Ni^{+} >$ control. A typical example of results is shown in Table III. The difference from the hydrated gels lies in presumably complete removal of water and a 14.3 times higher percentage of the metal salt. Tests have indicated the probability that the aquated ion is broken down by the dehydrating process. When amounts of metal salts in freeze-dried gels were decreased to the overall concentration that was present in the hydrated gels, relative catalytic activities were unchanged. Nickel was the only metal that kept its relative position in the activity scale. Nickel is similar to Co and Mn to the extent that higher valence states are extremely unstable and virtually nonexistent under acid aqueous conditions. However, this does not explain its inactivity in the freeze-dried samples.

Metal ions are no longer ionized due to the lack of water. Instead a relatively nonpolar environment now exists. This, as defined by Uri and coworkers (5), is a more favorable condition for catalysis by metals such as manganese and cobalt. From a practical standpoint, early investigators (14) have noted that catalysis by inorganic metal salts and metal soaps dispersed in vegetable oils was similar. Research by Karel and coworkers (15–19) on freeze-dried systems has indicated that water has a specific action on metal catalysts such as cobalt salts and acts as an antioxidant through aquation of metallic catalysts.

Catalytic Activity of Inorganic Metal Salts in Freezer-Stored Hydrated Gels

Autoxidation of hydrated gels containing metal salts (6.45×10^{-3} moles/20 g lard) stored at 24 F, 16 F and 0 F was examined. Oxidation was very slow; some means of increasing rate of autoxidation is needed for a more complete study. This might be done by the use of tocopherol-free lard and grinding the frozen gel. Typical results are shown in Table IV as found at the storage temperature of 24 F (−4.44 C). Catalysis was in the same order as observed in hydrated gels at 68 F (20 C). A possible exception may be Co^{++} which exhibited a positive catalytic activity that was not displayed at 20 C. In a physical sense, freezing is a dehydrating process, and this might account for the apparent increased relative activity of the Co^{++} ion. However, since Mn^{++} ion was the most active with dehydration, the pattern does not quite fit.

The behavior of the inorganic metal salts in the three physical states of the gel discussed above was in sharp contrast to the behavior of sodium chloride under similar conditions (2). This would appear to constitute further evidence that at least part of the sodium chloride prooxidant activity is not due to trace metals.

Catalysis by Organic Metal Compounds in Hydrated Gels at 20 C

Metal stearates were powerful catalysts and showed an order $Co^{++} > Mn^{++} > Fe^{++} > Cu^{++} > Ni^{++} > Sn^{++}$ = control nearly similar to that observed for the freeze-dried gels. The difference was in the order of Co^{++} and Mn^{++}. As shown in Table V, cobaltous stearate, the most powerful catalyst, exceeded the activity of ferrous chloride in the aqueous phase. Ferrous stearate was not quite as effective as ferrous chloride. Nickel stearate had very little catalytic activity. The investigations of Uri (4,5), concerning the influence of polarity of media, predict the above strong effect of cobaltous and manganous stearates. These stearates were found by Uri (5) to become more active as the solvent became less polar. The polar solvent causes solvation of the catalyst which alters its oxidation-reduction potential and affinity for molecular oxygen.

The effect of unbuffered pH variation from 5.0 to 6.7 on the performance of the metal stearates was examined. As might be predicted, changes in pH

had little influence on the catalytic activity of these compounds.

Monocarbonyl Compounds

Monocarbonyl determination was useful in interpreting results. As is known, and shown in Table I, peroxide values can be deceptive since they represent only one stage of the autoxidation process. Even the combination of peroxide and monocarbonyl values may not be infallible in deciding the degree and course of autoxidation. Some agents and conditions promoting hydroperoxide decomposition produce little monocarbonyl compounds. Kimoto and Gaddis (20) have shown that although some metal ions are powerful hydroperoxide decomposers, the yield of the monocarbonyl fraction may be very low. There is sometimes a large fraction of unidentified polar carbonyl compounds that has not been explored.

Monocarbonyl compounds formed in 1.5 cm thick hydrated gels by inorganic metal salts are shown in Table VI. Only Fe^{++} and Cu^{++} showed a positive prooxidant effect in this typical experiment. Ferrous ion produced the highest peroxide and monocarbonyl values and had an increase in the carbonyl-peroxide ratio with oxidation. Cupric ion, although prooxidant, produced lower amounts of monocarbonyls than the control. Cobaltous ion was apparently almost inert. Manganous ion, besides an apparent antioxidant effect, suppressed monocarbonyl formation even more than the Cu^{++} ion.

A similar study with stearates is shown in Table VII. Manganous stearate, although the second highest in rate of peroxide development, had a comparatively very low ratio of monocarbonyl formation. The cupric compound is again shown to be a poor monocarbonyl producer. Cobaltous stearate, the most effective prooxidant, had a relatively high efficiency in monocarbonyl formation.

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