Prooxidant Effects of Inorganic Chromium Compounds in the Autoxidation of Methyl Linoleate

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ABSTRACT AND SUMMARY

The prooxidant property of inorganic chromium compounds was determined in methyl linoleate free from natural antioxidants and metals. Prooxidant properties of inorganic chromium compounds appeared in order of sodium chromate > chromium (VI)-oxide > chromium chloride > potassium chromate > chromium (III)-oxide > potassium dichromate. In comparison with the control, additions of chromium compounds induced different amounts of autoxidation products derived from methyl linoleate, such as small amounts of hydroperoxides and conjugated dienes and large amounts of hydroxy groups, $\alpha,\beta,\gamma,\delta$-unsaturated carbonyls, isolated *trans* double bonds, polymers, and free radicals. From these analytical data, the catalysis of chromium compounds in the autoxidation of methyl linoleate seemed to be based on their abilities of abstracting a hydrogen from methyl linoleate and decomposing hydroperoxides derived from the autoxidation of methyl linoleate.

INTRODUCTION

Chromic acid oxidation of diphenylmethane (1), (+)-3-methylheptane (2), and alcohols (3) has been investigated by many workers. These works suggest that the initial reaction of chromic acid oxidation is the abstraction of a hydrogen from substrates forming a free radical as follows:

$$RH + Cr(VI) \rightarrow R\cdot + Cr(V) + H^+ \qquad (I)$$

In this case, chromium can take the transition from five to four or from four to three valent as well as that from six to five. Moreover, the catalysis of metalic compounds [having $M^{(n+1)+}$] in the autoxidation of various olefins has been known as follows (4):

$$ROOH + M^{n+} \rightarrow RO\cdot + M^{(n+1)+} + {}^-OH \qquad (II)$$

$$ROOH + M^{(n+1)+} \rightarrow ROO\cdot + M^{n+} + {}^+H \qquad (III)$$

Therefore, chromium compounds seem to promote the autoxidation of olefins through the reactions of equations I, II, III. In this report, inorganic chromium compounds are evaluated for their specific rolls in the autoxidation mechanism and for their effects upon the amount of products derived from the autoxidation of methyl linoleate.

EXPERIMENTAL PROCEDURE

Materials

The autoxidation substrate, methyl linoleate (ML, 99.9% purity as determined by gas liquid chromatography) was prepared from safflower fatty acids followed by the urea adducts formation, methyl esterification, and column chromatography with silicic acid to remove a trace of peroxides and pigments. Removal of natural antioxidants and metals from ML was confirmed by the ferric chloride: 2,2'-bipyridine method (5) and by atomic absorption spectra, respectively. The following chromium compounds were commercial products: sodium chromate (1, Guaranteed Reagent), chromium (VI)-oxide (2, Guaranteed Reagent), chromium chloride (3, Extra Pure Grade), potassium chromate (4, Guaranteed Reagent), chromium (III)-oxide (5, Guaranteed Reagent), and potassium dichromate (6, Guaranteed Reagent).

Autoxidation Procedure

Methyl linoleate (1.5000-1.5005 g) and chromium compounds (3.76×10^{-6} mole in the chromium unit) were added to beakers (4.1 cm diameter), respectively. The autoxidation of ML and the samples containing chromium compounds was carried out at 36.5 ± 0.5 C in an incubator under air atomosphere, after the volatile materials contained in the samples were removed for 1 hr at 30 ± 1 C under 10^{-3} mmHg pressure as described in the previous literature (6). Then the oil thickness in the beakers was 1.03 mm. The weight increase with the autoxidation of samples was determined by the weighing proceudre (7).

Analytical Procedure

Infrared ultraviolet (UV), and electron spin resonance (ESR) spectra, peroxide values (PV), molecular weights (MW) and refractive indices were determined on ML samples, with and without chromium compounds, from various autoxidation levels in order to examine the effects of chromium compounds on the autoxidation of ML. Infrared spectra were obtained with a Shimadzu IR-27B instrument and a grating IR spectrophotometer, Japan Spectro Scopic Co., (Tokyo, Japan) model DS-402G. Samples were diluted with carbon tetrachloride and run in 0.10 and 9.97 mm NaCl cells. The 9.97 mm NaCl cell was used to determine PV (8) due to the hydroperoxy group absorbing at 3520 cm^{-1} and due to the amount of hydroxy group (9) at 3600 cm^{-1}, in autoxidized samples which were diluted to 3.98 g/l for the IR analyses. The 0.10 mm NaCl cell was used to determine the amounts of (a) conjugated *cis,trans*- (at 948 cm^{-1}) and *trans,trans*-dienes (at 988 cm^{-1}) (10); (b) isolated *trans* double bond (at 968 cm^{-1}) (11); and (c) alpha methylene groups (at 3020 cm^{-1}), for autoxidized samples at 66.67 g/l concentration range. The absorption band at 3020 cm^{-1} in IR spectra has been assigned to alpha methylene groups by some workers, whereas it has been assigned to C-H of C=C-H by another workers. Privett et al (12) have shown in the study on the structure of hydroperoxides obtained from autoxidized methyl linoleate that the 3020 cm^{-1} band is assigned to the alpha methylene groups. Also, in this report, the 3020 cm^{-1} band was assigned to alpha methylene groups from comparison of IR spectra for various olefins. Moreover, the decrease in the active methylene proton signal at 2.80 ppm in NMR spectra accorded with that in the 3020 cm^{-1} band in IR spectra. The disappearance of active methylene groups was suggested by the appearance of conjugated dienes in IR and UV spectra for autoxidized ML samples. The streching vibrational band due to hydroperoxy groups appeared at 3450 cm^{-1} when observed by 0.10 mm NaCl cell, and appeared at 3520 cm^{-1} when observed by 9.97 mm cell. The 3520 cm^{-1} band was due to nonassociated hydroperoxy groups, and the 3450 cm^{-1} band to associated hydroperoxy groups. Peroxide values were calculated from the 3520 cm^{-1} band in IR spectra determined with 9.97 mm NaCl cell at the low concentration (3.98 g/l) of autoxidized samples, where hydropeoxides in the samples did not form intermolecular hydrogen bonds. Peroxide values (meq/Kg) were also measured by iodometry (13). Ultraviolet spectra were determined

TABLE I

The Effects of Chromium Compounds upon the Autoxidation Time (hr) to Gain the Constant Weight Increases in the Autoxidation of Methyl Linoleate[a]

Samples[b]	Weight increases (mg)							
	5	10	25	50	75	100	125	150
(1)	9.3	14.2	27.0	42.2	54.0	66.6	133.0	–
(2)	12.9	18.0	31.8	46.8	59.8	74.9	95.3	134.0
(3)	19.0	25.0	36.2	49.3	61.2	76.3	96.8	143.8
(4)	22.0	28.3	37.9	50.5	62.6	78.8	124.0	–
(5)	26.0	33.0	47.2	66.8	84.0	101.4	132.6	163.3
(6)	38.4	43.8	56.2	73.0	87.4	103.8	130.0	157.0
(7)	40.5	49.0	66.7	86.1	104.7	123.4	142.9	167.8

[a]Autoxidation temperature-36.5 ± 0.5 C, oil thickness-1.03 mm, concentration of chromium compounds—3.76 x 10^{-6} mole in the chromium unit.

[b](1), sodium chromate; (2), chromium (VI)-oxide; (3), chromium chloride; (4), potassium chromate; (5), chromium (III)-oxide; (6), potassium dichromate; (7), control. (1)-(7) are the same chromium compounds in later tables unless otherwise specified.

TABLE II

Relative Prooxidant Activities (RPA), Initial Rates of Weight Increases (IRWI), Maximum Rates of Weight Increases (MRWI), Maximum Weight Increases (MWI), and the Color Changes of Chromium Compounds (CCCC) in the Autoxidation of Methyl Linoleate Samples with and without Chromium Compounds

Samples	RPA[a]	IRWI[b] (mg/hr)	MRWI[c] (mg/hr)	MWI (mg)	CCCC
(1)	3.45	0.80	1.93	128	yellow-green
(2)	2.70	0.57	1.87	165	reddish purple-same color
(3)	1.96	0.30	2.00	159	green-same color
(4)	1.72	0.20	2.05	138	yellow-green
(5)	1.49	0.11	1.42	174	green-same color
(6)	1.12	0.01	1.49	170	orange-same color
(7)	1.00	0.01	1.21	174	–

[a]Shows the reciprocal of the ratios of induction periods in the samples with added chromium compounds to that in the control, where induction periods were specified to be the times (hr) required to gain the weight increases of 10 mg.

[b]The rates of weight increases until the autoxidized samples have the weight increases of 20 mg.

[c]Maximum rates of weight increases through the overall autoxidation reaction.

with a Shimadzu UV-200 instrument. Samples were diluted with methanol and were analyzed in a 1.00 cm quartz cell. The amounts of conjugated diene (14) and $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl were calculated from UV spectra. The detection and the quantitation of free radicals produced in the autoxidation of ML samples were carried out at 20 C using a ESR spectrometer, Japan Electron Optics Lab. Co., (Tokyo, Japan) model JES-1X. Samples were run in 5 mm diameter quartz tubes for ESR. Molecular weights were determined with a Hittachi Perkin-Elmer 115 type apparatus (by evaluating the vapor tension of sample solutions in benzene). Refractive indices were measured at 20 C with an Abbe refractometer.

RESULTS AND DISCUSSIONS

Weight increases with the autoxidation of ML samples containing chromium compounds of 3.76 x 10^{-6} mole in the chromium unit are shown in Table I. The additions of chromium compounds promoted the autoxidation of ML. These prooxidant activities were compared at the time (hr) required to gain 10 mg weight increase that was generally regarded as the end point of the induction period in all samples. These induction periods are shown in the 10 mg weight increase point of Table I. The relative prooxidant activities of chromium compounds to the control were calculated from the comparison of these induction periods and shown in Table II. The initial rates of weight increases until the autoxidized samples have 20 mg weight increase, the maximum rates of weight increases through the overall autoxidation process, and the maximum autoxidation weight increases are also given in Table II. As noted in the relative prooxidant activities and the initial rates of weight increases of Table II, the prooxidant properties of chromium compounds appeared in order of (1) > (2) > (3) > (4) > (5) > (6). However the data of maximum weight increase rates through the overall autoxidation process show the similar proooxidant properties in (1), (2), (3), and (4). Therefore, the different prooxidant properties between these chromium compounds are likely due to the different initial rate of weight increases. The low prooxidant properties of (5) and (6) seem to be due to the relative low initial rate and the low maximum rate of weight increases to other chromium compounds. The maximum weight increases in the autoxidation of ML samples, as shown in Table II, were generally controlled to the low values by additions of chromium compounds, and especially by additions of (1) or (4). The lower maximum weight increases in the samples with added chromium compounds in comparison with the control seem to be due to the larger formations of polymeric products as a result of catalytic decomposition of ML hydroperoxides with chromium compounds. The chromium compounds changed their color in the autoxidation of ML as shown in Table II. However, the color of chromium compounds recovered from autoxidized samples showed the original color when they were dissolved in water. At any rate, the color change of chromium compounds in autoxidized ML samples seems to be based on the change of electron charge of chromium.

The analyses of autoxidation products derived from ML

TABLE III

The Effects of Chromium Compounds upon the Amounts of: A, Alpha Methylene Groups (%) Calculated from IR Spectra; B, Peroxide Values (x 10^3 meq/Kg) Measured by Iodometry; C, Peroxide Values (x 10^3 meq/Kg) Calculated from IR Spectra; D, Hydroxy Groups (%) Calculated from IR Spectra, in the Autoxidation of Methyl Linoleate

		Weight increases (mg)							
	Samples	5	10	25	50	75	100	125	150
A	(1)	90.9	83.5	64.7	46.1	28.9	13.2	7.0	–
	(2)	91.1	82.9	65.7	46.0	29.7	22.7	14.8	4.6
	(3)	91.9	83.6	64.7	45.1	30.2	22.2	15.2	10.1
	(4)	91.6	83.7	65.1	45.3	30.7	22.3	14.1	–
	(5)	91.7	84.5	63.9	45.6	31.0	23.2	15.1	10.6
	(6)	91.6	83.0	64.3	46.7	30.7	23.2	15.0	10.1
	(7)	91.3	83.6	64.7	46.0	30.0	22.8	14.8	9.8
B	(1)	0.27	0.49	0.94	1.39	1.71	1.78	1.78	–
	(2)	0.23	0.46	0.97	1.92	2.79	3.09	3.22	3.22
	(3)	0.24	0.47	1.06	2.22	3.20	3.77	3.88	3.62
	(4)	0.26	0.52	1.07	1.84	2.35	2.43	2.35	–
	(5)	0.25	0.50	1.14	2.12	2.90	3.68	3.89	3.66
	(6)	0.27	0.50	1.16	2.18	2.93	3.42	3.79	3.62
	(7)	0.25	0.49	1.20	2.30	3.00	3.45	3.83	4.13
	(8)	0.19	0.37	0.94	1.87	2.81	3.74	4.68	5.61
C	(1)	0.27	0.52	1.10	1.44	1.58	1.62	1.48	–
	(2)	0.26	0.51	1.12	1.91	2.25	2.40	2.31	2.09
	(3)	0.26	0.52	1.20	2.14	2.48	2.40	2.17	1.92
	(4)	0.26	0.52	1.26	1.93	2.26	2.04	1.82	–
	(5)	0.26	0.52	1.23	2.05	2.43	2.70	2.74	2.31
	(6)	0.26	0.51	1.24	2.20	2.52	2.60	2.46	2.24
	(7)	0.26	0.51	1.23	2.29	2.61	2.83	2.84	2.72
D	(1)	0.00	0.00	0.00	0.00	0.01	0.16	0.46	–
	(2)	0.00	0.00	0.00	0.00	0.00	0.12	0.36	0.66
	(3)	0.00	0.00	0.00	0.00	0.00	0.06	0.21	0.46
	(4)	0.00	0.00	0.00	0.03	0.09	0.22	0.49	–
	(5)	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.18
	(6)	0.00	0.00	0.00	0.00	0.00	0.01	0.10	0.41
	(7)	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.10
	(8)	shows theoretical values.							

samples with and without chromium compounds offered some informations about the autoxidation mechanism of ML catalyzed by chromium compounds. The autoxidation mechanism of olefins has been generally proposed as follows (15,16):

$$RH + O_2 \rightarrow R\cdot + \cdot OOH \quad (IV)$$

$$R\cdot + O_2 \rightarrow ROO\cdot \quad (V)$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot \quad (VI)$$

$$ROOH \rightarrow RO\cdot + \cdot OH \quad (VII)$$

$$RO\cdot + RH \rightarrow ROH + \cdot R \quad (VIII)$$

Various termination reactions are induced by the coupling and the disproportionation of free radicals (IX).

Infrared spectra observed by 0.10 mm NaCl cell for autoxidized samples with and without chromium compounds showed increases (I) or decreases (D) in the following absorption bands: hydroxy (I), hydroperoxy (I), alpha methylene (D), aldehyde (I) at 1725 cm^{-1}, ketone (I) at 1715 cm^{-1}, active methylene (D) at 1400 cm^{-1} (the increase of the absorption band between 1400-1100 cm^{-1} was due to the formation of polymeric products), cyclic peroxide (I) at 1100 cm^{-1}, conjugated *trans,trans* diene (I), conjugated *cis,trans* diene (I), conjugated diene (I) at 1650 and 1600 cm^{-1}, isolated *trans* double bond (I) and isolated *cis* double bond (D) at 913 cm^{-1}. Formations of aldehyde (1725 cm^{-1}) functional groups were negligible even in highly autoxidized ML samples. Informations obtained from the IR spectra for the samples with and without chromium compounds suggest that the autoxidation of ML is induced by the dehydrogenation of the active methylene group (as shown in the decrease of the 3020 cm^{-1} band in IR spectra and that of the active methylene proton signal at 2.80 ppm in NMR spectra), located between the two double bonds, leading to the accumulation of hydroperoxides, as well as the formation of conjugated *cis,trans* diene and its transformation to conjugated *trans,trans* diene, and that of polymeric and ketonic products. However, the additions of chromium compounds induced the different amounts of autoxidation products from ML in comparison with the control. The diminution of the alpha methylene groups (3020 cm^{-1}) with autoxidation weight increases is shown in Table IIIA. The decrease in the alpha methylene content of autoxidized samples was confirmed by noting a corresponding decrease in the active methylene proton signal at 2.80 ppm in NMR spectra. Therefore, IR data seem to show the disappearance of the active methylene group which is one of alpha methylene groups in ML samples. The addition of chromium compounds shortened the time in proportion to their prooxidant abilities (see Table I and II), compared to the control, when the alpha methylene content began to decrease. But, as noted in Table IIIA, the decrease in the alpha methylene content of the samples with added chromium compounds was similar to that of the control in comparison at the same autoxidation level. These results show that autoxidation of ML samples with and without chromium compounds have the same loss in the alpha methylene content during autoxidation for the same weight increase. The effects of chromium compounds on the PV formation in oxidized ML samples are shown in Table IIIB and C. The low value of IR spectra data, compared to the iodometric data, was based on the fact that the IR spectra data about PV did not include the hydroperoxides forming intramolecular hydrogen bonds as described in the experimental section. The change of the difference between both PV approximately parallel with the increase of polymeric products in autoxidized ML sam-

TABLE IV

The Effects of Chromium Compounds upon the Amounts of: A, Conjugated Dienes (%) Calculated from UV Spectra; B, *cis,trans* and C, *trans,trans* Conjugated Dienes (%) Calculated from IR Spectra; and D, Free Radicals (x 10^{-7} mole/1.5 g Methyl Linoleate), Derived from the Autoxidation of Methyl Linoleate

	Samples	Weight increases (mg) 5	10	25	50	75	100	125	150
A	(1)	3.1	6.3	9.0	14.3	18.4	20.6	15.0	–
	(2)	3.2	6.2	8.7	14.8	19.8	22.2	20.4	16.4
	(3)	3.3	6.3	9.1	14.9	19.0	21.0	20.6	17.7
	(4)	3.1	6.3	8.8	15.0	18.5	19.4	15.8	–
	(5)	3.7	6.2	8.6	15.2	20.6	24.2	24.2	21.6
	(6)	3.9	5.7	8.8	15.5	20.6	24.2	20.8	19.3
	(7)	3.1	6.2	8.6	15.1	20.2	23.8	24.8	22.1
B	(1)	1.21	2.14	6.08	6.35	4.53	3.52	2.11	–
	(2)	1.30	2.20	6.38	6.49	5.12	3.73	2.88	2.02
	(3)	1.23	2.13	6.10	6.55	4.63	3.93	2.73	2.09
	(4)	1.26	2.15	6.20	6.57	5.16	4.04	2.98	–
	(5)	1.27	2.26	6.37	6.62	5.28	4.19	3.10	2.21
	(6)	1.28	2.17	6.42	6.68	5.22	4.27	3.26	2.22
	(7)	1.24	2.19	6.46	6.63	5.28	4.29	3.22	2.29
C	(1)	1.71	2.91	5.16	5.76	6.03	5.18	2.97	–
	(2)	1.81	2.93	5.20	6.98	7.58	7.49	6.30	4.29
	(3)	1.77	2.96	5.26	7.03	8.31	9.24	6.49	4.01
	(4)	1.78	2.92	5.17	6.26	7.11	7.88	5.52	–
	(5)	1.70	2.96	5.36	7.19	8.43	8.78	6.23	4.14
	(6)	1.75	2.95	5.41	7.22	8.61	9.34	6.59	4.03
	(7)	1.70	2.95	5.36	7.12	8.65	9.38	6.69	4.34
D	(1)	3.22	4.29	6.08	7.02	7.31	7.17	6.85	–
	(2)	–	–	–	–	–	–	–	–
	(3)	–	–	–	–	–	–	–	–
	(4)	2.30	3.28	4.81	5.93	6.67	7.00	6.39	–
	(5)	2.00	2.75	3.95	5.01	5.58	5.88	6.12	6.16
	(6)	1.86	2.56	3.72	4.92	5.60	6.01	6.17	6.18
	(7)	1.70	2.36	3.53	4.56	5.36	5.76	6.05	6.14

ples as shown in the quantitative change of molecular weights and isolated *trans* double bonds. Calculating the theoretical data, it was assumed that the oxygen absorbed during autoxidation (weight increases) was quantitatively related to hydroperoxide formations. The correlation between weight increases and PV for the control samples agreed with the theoretical data until the autoxidized ML had weight increases of 85 mg or a PV of 3.2 x 10^3 meq/Kg as determined from iodometry measurements, and 63 mg or 2.3 x 10^3 meq/Kg as determined from IR spectra. But, from ML samples with added chromium compounds, the above corresponding values are only ca. 25 mg in the correlations from both iodometry and IR data. This fact suggests that the amount of oxygen absorbed in the samples was quantitatively used to form hydroperoxides until the autoxidized ML had weight increases of 85 mg or a PV of 3.2 x 10^3 meq/Kg for the control samples, and weight increases of 25 mg or a PV of 0.94 x 10^3 meq/Kg for samples with added chromium compounds. Therefore, the reactions represented by equations VII and VIII would be negligible in these autoxidation range. Hence, the catalyses (equations II and III) of chromium compounds on the decomposition of hydroperoxides seem to be negligible until the samples with added chromium compounds had autoxidation weight increases of about 25 mg. These facts suggest that the autoxidation of ML samples (from 0.0 to 25.0 mg of weight increases) catalyzed by chromium compounds is induced mainly by the hydrogen abstraction reaction (equation I). Therefore, the different initial rate of weight increases, shown in Table II, might reflect the different abilities of chromium compounds in the hydrogen abstraction reaction as shown in equation I. However, at the autoxidation level of over 25 mg weight increases, the catalyses (shown in equations II and III) of chromium compounds on the decomposition of hydroperoxides were observed in all used chromium compounds, especially in (1) and (4) as shown in the low PV in Table IIIB and C. The quantitative data of hydroxy groups in the samples with and without chromium compounds are shown in Table IIID. The additions of chromium compounds to ML induced the large amount of hydroxy groups in comparison with the control. The large amounts of hydroxy groups in the samples with added chromium compounds seem to result from the catalytic decomposition of hydroperoxides by chromium compounds (see equations II and VIII).

Conjugated diene contents calculated from UV spectra of ML samples with and without chromium compounds are shown in Table IVA. The conjugated *cis-trans-* and *trans, trans*-diene contents calculated from IR spectra for the samples with and without chromium compounds are shown in Table IIIB and C, respectively. The amounts of conjugated dienes calculated from UV spectra and those of conjugated *trans,trans* dienes increased with the autoxidation of ML samples and had the maximum value at the weight increases of ca. 100 mg. On the other hand, conjugated *cis,trans* diene is formed first to have their maximum values in autoxidation of ML samples, then with increasing of weight they convert to conjugated *trans,trans* diene configurations. This phenomenon of *cis,trans* ceding to the *trans,trans,* configuration is confirmed from UV evidence in that the absorption maximum (λ_{max}) for conjugated dienes contained in the autoxidized samples shifted from 233 to 231 nm with increasing autoxidation time. As noted in Table IVA, B, and C, formations of conjugated dienes were similar to that of the control until the autoxidized ML samples had weight increases of about 25 mg but, at the autoxidation level of over 25 mg weight increase, they were generally controlled to the low values by the additions of chromium compounds, especially by the additions of (1) or (4). The small amounts of conjugated dienes for the samples with added chromium compounds seem to be due to the large formations of polymeric products as the result of catalytic decomposition of ML hydroperoxides with chromium compounds.

TABLE V

The Effects of Chromium Compounds upon the Amounts of: A, Isolated *trans* Double Bonds (%) Calculated from IR Spectra; B, Molecular Weights, C, $\alpha,\beta,\gamma,\delta$-Unsaturated Carbonyl (1 g/cm); and D, Refractive Indices (20 C), in the Autoxidation of Methyl Linoleate

		Weight increases (mg)							
	Samples	5	10	25	50	75	100	125	150
A	(1)	0.00	0.00	0.00	0.00	0.80	1.80	4.80	–
	(2)	0.00	0.00	0.00	0.00	0.80	1.86	2.33	3.01
	(3)	0.00	0.00	0.00	0.00	0.66	1.30	1.96	5.05
	(4)	0.00	0.00	0.00	0.00	0.50	2.28	4.01	–
	(5)	0.00	0.00	0.00	0.00	0.70	1.59	2.41	3.21
	(6)	0.00	0.00	0.00	0.00	0.50	1.01	1.69	2.40
	(7)	0.00	0.00	0.00	0.00	0.47	0.98	1.53	2.23
B	(1)	295	296	303	328	365	404	448	–
	(2)	294	295	300	321	352	388	427	469
	(3)	294	295	301	320	348	382	419	466
	(4)	294	295	301	327	360	399	447	–
	(5)	294	294	296	307	338	366	402	446
	(6)	294	294	296	307	338	366	395	432
	(7)	294	294	296	307	338	366	395	431
C	(1)	0.00	0.00	0.96	2.12	2.89	2.27	0.89	–
	(2)	0.00	0.00	0.00	0.22	0.49	0.79	0.74	0.42
	(3)	0.00	0.00	0.00	0.11	0.34	0.66	0.72	0.40
	(4)	0.00	0.00	0.58	1.19	1.98	1.75	1.21	–
	(5)	0.00	0.00	0.00	0.08	0.14	0.19	0.25	0.36
	(6)	0.00	0.00	0.00	0.07	0.14	0.18	0.23	0.28
	(7)	0.00	0.00	0.00	0.08	0.14	0.19	0.24	0.27
D	(1)	1.4634	1.4651	1.4680	1.4690	1.4691	1.4727	1.4769	–
	(2)	1.4629	1.4640	1.4665	1.4691	1.4707	1.4724	1.4744	1.4775
	(3)	1.4627	1.4635	1.4649	1.4673	1.4698	1.4723	1.4748	1.4773
	(4)	1.4625	1.4635	1.4664	1.4704	1.4723	1.4731	1.4739	–
	(5)	1.4634	1.4649	1.4667	1.4690	1.4700	1.4715	1.4736	1.4762
	(6)	1.4628	1.4638	1.4665	1.4685	1.4692	1.4712	1.4745	1.4776
	(7)	1.4634	1.4640	1.4661	1.4694	1.4733	1.4753	1.4762	1.4769

The change of the free radical (g-value = 2.00611) concentration in ML samples with respect to autoxidation weight increases is shown in Table IVD. The free radical species might be the peroxy radicals due to equation V until the autoxidized samples had weight increases of 85 mg or a PV of 3.2×10^3 meq/Kg for the control samples, and weight increases of ca. 25 mg or a PV of 0.94×10^3 meq/Kg in samples with added chromium compounds. That they are peroxy radicals is based upon data in Table IIIB, where the agreement of the correlation between weight increases and PV with theoretical data was observed. Table IVD appears to show that the free radical formations increases linearly from the initial autoxidation stage of the induction periods, then deviate from its linearity. The decrease in the free radical formation near the maximum values probably results from the polymerization due to the coupling of free radicals and from the reduced chain propagation rate due to the decline in the concentration of ML. In comparison to the control the addition of chromium compounds to ML induced the large formations of free radicals in parallel with their prooxidannt activities on the autoxidation of ML (Tables I and II). The large free radical formations of the samples with added chromium compounds seem to be due mainly to the hydrogen abstraction reaction by chromium compounds, as shown in equation I, until the autoxidized samples had the weight increases of 25 mg. Still the free radical content of ML samples with added (2) or (3) was not quantitatively detected by reason of the paramagnetic properties of these chromium compounds. Other significant observations on the oxidation of ML include data on isolated *trans* double bond calculated from IR spectra, the average MW of oxidized ML, the $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl content (λ_{max} = 272 nm) calculated from UV spectra, and refractive indices; the data are shown in Table VA, B, C, and D, respectively. These additional results show that the additions of chromium compounds to ML derive large amounts of polymerized and unsaturated carbonyl products. Even then, compared to the control, additions of chromium compounds to ML resulted in the formations of large amounts of hydroxy and unsaturated carbonyl products and free radicals derived from the autoxidation of ML, and those of small amounts of maximum autoxidation weight increases, hydroperoxides, and conjugated dienes. All of the analytical data show that the catalyses of chromium compounds on the autoxidation of ML are based on their abilities to abstract a hydrogen from ML and to decompose hydroperoxides derived from the autoxidation of ML.

REFERENCES

1. Wiberg, K.B., and R.J. Evans, Tetrahedron 8:313 (1960).
2. Wiberg, K.B., and G. Foster, J. Am. Chem. Soc. 83:423 (1961).
3. Martiney, A.M., G.E. Cushmac, and J. Rocek, Ibid. 97:6502 (1975).
4. Pryor, W.A., "Free Radicals," McGraw-Hill Book Co., New York, 1966, P. 136.
5. Mehlenbacher, V.C., "The Analysis of Fats and Oils," Swift & Co., Chicago, 1960, p. 586.
6. Fukuzumi, K., and N. Ikeda, JAOCS 46:64 (1969).
7. Olcott, H.S., and E. Einset, Ibid. 35:161 (1958).
8. Fukuzumi, K., and E. Kobayashi, Ibid. 49:162 (1972).
9. Ahlers, N.H.E., and N.G. McTaggart, Analyst 79:70 (1954).
10. Chipault, J.R., and J.M. Hawkins, JAOCS 36:535 (1959).
11. AOCS Tentative Method Cd:14-61, AOCS, Chicago, Second Edition, 1959.
12. Privett, O.S., W.O. Lundberg, N.A. Khan, W.E. Tolberg, and D.H. Wheeler, JAOCS 30:61 (1953).
13. Privett, O.S., W.O. Lundberg, and C. Nickell, Ibid. 30:17 (1953).
14. AOCS Official Method Cd:7-58, AOCS, Chicago, Second Edition, 1962.
15. Pryor, W.A., "Free Radicals," McGraw-Hill Book Co., New York, 1966, p. 290.
16. Bateman, L., Quart, Rev., 8:147 (1954).

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