The Effect of Antioxidants in the Autoxidation of Methyl Conjugated *Cis, Trans*-Octadecadienoates

KAZUO FUKUZUMI and NOBUO IKEDA, Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya, Japan

Abstract

The effect of antioxidants on the autoxidation of methyl conjugated *cis,trans*-octadecadienoates was evaluated by estimating the induction period by measuring the increase in weight with time. Peroxide values and molecular weights were also used to determine extent of oxidation. UV and IR absorption were measured to determine conjugated dienes and isolated *trans* double bonds. Antioxidants, such as butylated hydroxy anisole (BHA), butylated hydroxy toluene (BHT), propyl gallate (PG) and sesamol, lengthened the induction period as much as seven to twelve times. After autoxidation to a weight gain of 10 mg per 1.5 g, the antioxidant containing samples had higher molecular weights and lower diene contents than the control samples. The induction periods were shorter, the peroxide values lower with or without antioxidants for the conjugated dienoates than for the nonconjugated dienoates. Effect of antioxidants might be explained by the formation of a hydrogen bond of the hydroxyl of the antioxidant and π-electrons as well as the inhibition of the chain-reaction.

Introduction

In the previous paper on the effect of antioxidants in the autoxidation of methyl nonconjugated octadecadienoates (1), it was found that the *cis,cis*-isomer was more easily autoxidized and had a shorter induction period than the *trans,trans*-form. By the end of the induction period, no isolated *trans* double bond forms in the *cis,cis*-isomer, but a considerable amount of isolated *trans* double bond decreased in the *trans,trans*-isomer. In general, the effects of antioxidants except NDGA on the *cis,cis*-isomer were larger than the *trans,trans*-form. But the effects of antioxidants on the position isomers of polyenoates, especially conjugated ones, have never been investigated. Methyl conjugated *cis,trans*-octadecadienoates were used as the sample, and butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), nordihydroguaiaretic acid (NDGA), 4,4′-dihydroxy-3,5,3′,5′-tetra-tert-butyl diphenyl methane, L-thyroxine sodium salt, α-tocopherol and sesamol as antioxidants. The effect of antioxidants was examined by measuring the induction period by the weight gain method. The IR and UV spectra, peroxide values, conjugated diene contents, isolated trans double bond contents and molecular weights were determined for the controls and the samples containing antioxidants.

Experimental Procedure

Materials

Methyl conjugated *cis,trans*-octadecadienoates (97% purity as determined by UV) were prepared from the methyl ester of safflower fatty acids followed by the urea adduct formation and the alkali-isomerization (2). The removal of natural antioxidants from the dienoates was confirmed (3). Antioxidants, such as BHA, BHT, PG, NDGA, α-tocopherol, L-thyroxine sodium salt and sesamol were commercial products, and 4,4′-dihydroxy-3,5,3′,5′-tetra-tert-butyl diphenyl methane (mp 154.2–154.6 C; 154 C (4)), a synthetic product.

Autoxidation Procedure (5,6)

The autoxidation of methyl conjugated *cis,trans*-octadecadienoates and the samples containing the antioxidants (0.01% on the basis of the conjugated dienoates) was carried out by the procedure described in the previous paper (1).

The weight increase in the autoxidation of the samples was determined by the weighing procedure (5,6). The weight gain chosen as the end of the induction period was 10 mg per 1.5 g as in the previous paper (1). IR spectra were determined with a usual NaCl prism type, the Schimazu IR-27B apparatus, with a 0.1 mm NaCl cell, and with carbon tetrachloride and carbon disulfide as solvents. Peroxide values (m.eq./kg.) were measured by the iodometry (7). Conjugated *cis,trans*-diene contents were estimated from the result of the IR spectra. Isolated *trans* double bond contents were also calculated from the IR spectra. Molecular weights were measured with the Hitachi Perkin-Elmer 115 type apparatus for molecular weight determination (by evaluating the vapor tension of sample solutions in benzene).

Results and Discussion

For methyl conjugated *cis,trans*-octadecadienoates and each sample containing the antioxidant, the autoxidation induction period was determined. The results are given in Table I. BHA, BHT and sesamol extended the induction period almost 12 times. The induction periods for methyl conjugated *cis,trans*-octadecadienoates are shorter than for methyl 9-*cis*, 12-*cis*-octadecadienoate (1).

IR spectra for the sample and for those gaining 10 mg and 50 mg (containing BHT) per 1.5 g were similar among those for the samples containing no or any antioxidants, but there was the difference in the specific extinction coefficient among them. The weak absorption band due to the –OOH at 3450 cm^{-1} for the samples gaining 10 mg or 50 mg per 1.5 g was smaller than that for the nonconjugated octadecadienoates (1). The *cis,trans*-conjugated diene absorption bands at 982 and 948 cm^{-1} for the samples gaining 10 or 50 mg per 1.5 g were weaker than those for the original sample. There was scarcely any

TABLE I

Effect of Antioxidants on the Induction Period in the Autoxidation of Methyl Conjugated *Cis,Trans*-Octadecadienoates

Antioxidant	Induction period (hr)	Effect (ratio)[a]	Ratio[b]
Control	16	1	0.46
BHA	190	12(11.9)	0.95
BHT	190	12(11.9)	0.66
PG	110	6.9	0.20
NDGA	40	2.5	0.57
D[c]	68	4.3	0.34
L-Thyroxine	17	1.1	0.14
α-Tocopherol	44	2.8	0.98
Sesamol	190	12(11.9)	0.59

[a] Ratio of induction period of sample containing antioxidant to blank control.
[b] Ratio of induction period of *cis,trans*-conjugated dienoates to that of *cis,cis*-nonconjugated dienoate (1).
[c] 4,4′-Dihydroxy-3,5,3′,5′-tetra-tert-butyl diphenyl methane.

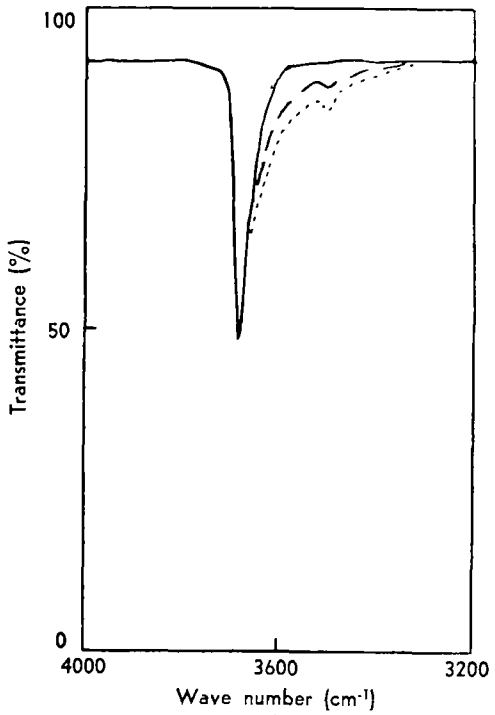

FIG. 1. IR spectra for BHT (———), BHT with methyl linoleate (1:1 mole) (— — —), and BHT with methyl conjugated *cis,trans*-octadecadienoates (1:1 mole) (– – – – – – – –).

absorption band for the isolated *trans* double bond at 968 cm^{-1} in the samples gaining 10 mg, but a shoulder in those gaining 50 mg per 1.5 g.

Peroxide values (m.eq./kg.), the increase of molecular weight (%) and the decrease of conjugated diene (%) are shown in Table II. A gain of 10 mg/1.5 g weight in the sample corresponds to the absorption of 6.8 mole per cent oxygen, because no volatile matter, such as ketones and aldehydes, is found in the IR spectra. In practice, the shape of the absorption band in the samples gaining 10 mg per 1.5 g at 1725–1665 cm^{-1} (caused by saturated and unsaturated aldehydes and ketones) was the same as that in the original sample. If aldehydes and ketones are present in small amounts, the absorption band for them must be broad. When practically no volatile matters are present, as in the induction period, oxygen absorption can be estimated by the weight gain method. 6.8 Mole per cent oxygen is nearly 5.2–6.0 mole per cent of the –OOH group. Therefore, the absorbed oxygen predominantly forms the —OOH group. As shown in Table II, the peroxide value for the *cis,trans*-conjugated dienoate is smaller than for the *cis,cis*-nonconjugated dienoate (1). The increase of molecular weight and decrease of conjugated diene are greater for the conjugated dienoate containing antioxidants at the end of the induction period of autoxidation than for the blank control.

The reason for longer induction periods in the autoxidation of the samples containing the antioxidants than that in the control results from the inhibition of the chain reaction by the antioxidants, as in the nonconjugated dienoate (1). An additional reason may be that hydrogen bonds are formed between the –OH group of the antioxidants and π-electrons of double bonds of the samples (8–10). This evidence is given in Figure 1. In this experiment, IR spectra were determined with the above-mentioned apparatus and with carbon tetrachloride as a solvent.

In addition to the OH absorption at 3670 cm^{-1}, a new band appears near 3480 cm^{-1} as a result of

TABLE II

Oxidation of Methyl Conjugated *Cis,Trans*-Octadecadienoates

Antioxidant	Peroxide value (m.eq./kg.)	Mole % of –OOH	Ratio[a]	Increase of molecular weight, % (Dimer, %)	Decrease of conjugated diene, %
Control	320	5.2	0.64	9.6	20
Sesamol	330	5.4	0.74	15.7	28
BHA	350	5.7	0.70	12.1	24
BHT	370	6.0	0.77	11.1	24

[a] Ratio of peroxide value for the *cis,trans*-conjugated dienoate to that for the *cis,cis*-nonconjugated dienoate (1).

hydrogen bonding. This is especially evident in the IR spectrum for the mixture of BHT with methyl conjugated *cis,trans*-octadecadienoates. It has been confirmed that the formation of hydrogen bonds gives rise to the OH stretching frequency shift to the lower wave number (11). A small shift and broadness in OH stretching with the mixture of BHT and the conjugated dienes in equimolar concentrations are detectable in IR spectroscopic evidence as mentioned above. Thus, the hydrogen-bonding may also exist in the very small concentration of antioxidants (0.01%) as in this study. The detection by IR spectroscopy becomes very difficult because the amount of the reactant (the conjugated dienes) is much larger than the antioxidant and unlike the equimolar concentrations shown in Figure 1.

$$\begin{array}{l} \overset{\delta+}{} \\ -CH=CH=CH=CH- \\ \quad\vdots \\ \quad H \\ \quad A \end{array} \qquad \text{HA: Antioxidant}$$

On the opposite side of the hydrogen bond, the electronic density of the conjugated diene becomes lower, and the attack of oxygen (electrophilic) at the double bond becomes more difficult. Thus, the antioxidants may retard the induction period of the conjugated diene. The following mechanism of the autoxidation of conjugated polyethenoid compounds was proposed by Allen and Kummerow (12).

$$-CH=CH-CH=CH-CH=CH- + O_2 \rightarrow$$
$$-CH=CH-CH=CH-\underset{\cdot}{CH}-CH-$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad O$$
$$\qquad\qquad\qquad\qquad\quad O$$
$$\qquad\qquad\qquad\qquad\quad \cdot$$

Therefore, the attack of oxygen at conjugated double bonds as mentioned above may be reasonable, especially in the absence of antioxidant.

The increase of the molecular weight of the conjugated dienoates in the induction period of autoxidation may arise from the termination between radicals, though the detailed mechanism is still obscure.

The effect of antioxidants in the autoxidation of methyl conjugated *cis,trans*-octadecadienoates is the retardation of the induction period and the slight facilitation of polymerizations in the early stage of autoxidation.

REFERENCES

1. Fukuzumi, K., and N. Ikeda, JAOCS *46*, 64 (1969).
2. Nichols, Jr., P. L., S. F. Herb and R. W. Riemenschneider, J. Am. Chem. Soc. *73*, 247 (1951).
3. Mehlenbacher, V. C., "The Analysis of Fats and Oils," The Garrard Press, Champaign, Ill., 1960, p. 586.
4. Kharasch, M. S., and B. S. Jochi, J. Org. Chem. *22*, 1437 (1957).
5. Olcott, H. S., and E. Einset, JAOCS *35*, 159 (1958).
6. Olcott, H. S., and E. Einset, Ibid. 161 (1958).
7. Privett, O. S., W. O. Lundberg and C. Nickell, Ibid. *30*, 17 (1953).
8. Baker, A. W., and A. T. Schulgin, J. Am. Chem. Soc. *80*, 5358 (1958); *81*, 4525 (1959).
9. Baker, A. W., and A. T. Schulgin, Ibid. *81*, 4525 (1959).
10. West, R., Ibid. *81*, 1614 (1959).
11. Coley, R. T., "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, p. 118.
12. Allen, R. R., and F. A. Kummerow, JAOCS *28*, 101 (1951).

[Received June 17, 1969]