

# CHAPTER 7

## Oxidation\*

### A. OXIDATION BY OXYGEN

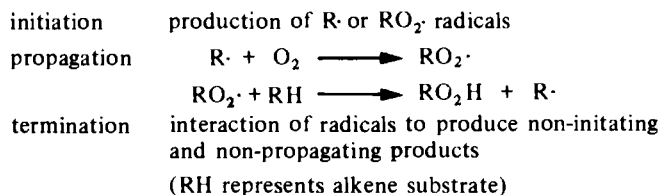
#### 1. Introduction

Oxidation of olefinic compounds by atmospheric oxygen is important in the development of rancidity, in the production of desirable and undesirable flavours, in the polymersiation of highly unsaturated (drying) oils, and in the production of compounds of significant physiological activity. These changes, which may or may not require enzymes, result from complex reactions in complicated substances often under undefined conditions and understanding of the processes involved has developed from the study of simpler substrates such as methyl oleate, linoleate, or linolenate.

Reaction between olefin and oxygen probably requires the activation of the alkene or of the oxygen, and the two processes follow different pathways to slightly different products. The first isolable oxidation products are unsaturated hydroperoxides which undergo further reaction to produce compounds of lower molecular weight after chain fission, compounds of similar molecular weight, and compounds of higher molecular weight after dimerisation or polymerisation.

#### 2. Autoxidation<sup>1,2†</sup>

The major non-enzymic oxidation process is a radical chain reaction involving initiation, propagation, and termination steps (Scheme 7.1).



SCHEME 7.1. Autoxidation of the alkene RH, where H represents an allylic hydrogen.

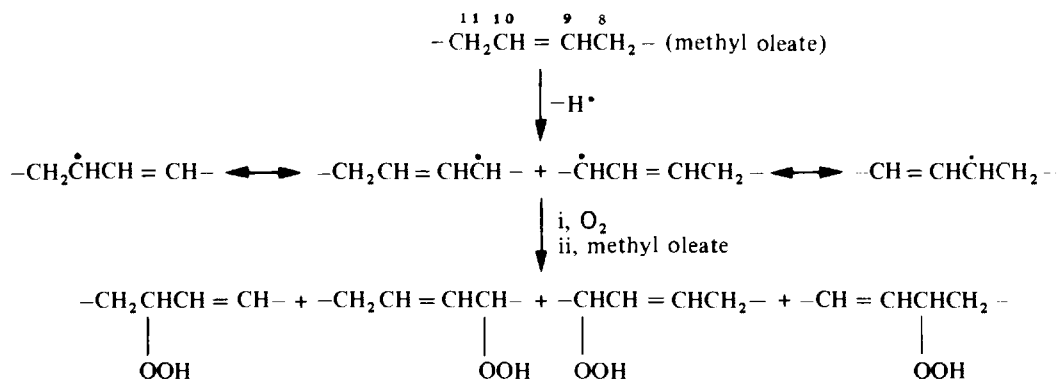
\* See also Chapter 19.

† Superscript numbers refer to References at end of Chapter.

The nature of the initiation reaction is still uncertain, though it is known that hydroperoxides once formed furnish additional initiating radicals. The reaction of alkenes with singlet oxygen (Section 3) to produce hydroperoxides may play a key role in the initiation of autoxidation. The propagation sequence involves the production of a radical  $R\cdot$  from the alkene  $RH$  and its subsequent reaction with oxygen. The radical results from the alkene by reaction at the allylic position and is resonance-stabilised. This affects the structure of the final product. The termination reactions have not been extensively studied.

Autoxidation is facilitated by pro-oxidants and inhibited by antioxidants. Pro-oxidants, such as metals or other radical initiators, operate by promoting the initiation step in the chain reaction or they may inhibit the activity of antioxidants. Antioxidants are frequently added to fats and to fat-containing foodstuffs to prolong shelf-life. These are often phenolic compounds, but only approved substances may be added to materials which are to be eaten. Such compounds interfere with the propagation sequence by converting propagating radicals into non-propagating species. Their effectiveness is often increased by compounds such as citric acid, ascorbic acid, or phosphoric acid (called synergists), all of which inhibit the initiation step by removal of metallic impurities which otherwise act as pro-oxidants. Photo-oxidation is inhibited by singlet oxygen quenchers such as carotene. (For further discussion see Chapter 19.)

Autoxidation of pure methyl oleate (in particular, oleate which is free of linoleate) is a slow reaction, occurring only after a long induction period. This can be shortened by addition of a radical source, by irradiation, or by raising the temperature. Samples of oleate containing linoleate also have shorter induction periods because the more readily formed products of linoleate oxidation can initiate oleate oxidation. The hydroperoxides produced from methyl oleate are a mixture of the *cis* and *trans* isomers of 8-hydroperoxy  $\Delta^9$ -, 9-hydroperoxy  $\Delta^{10}$ -, 10-hydroperoxy  $\Delta^8$ -, and 11-hydroperoxy  $\Delta^9$ -octadecenoates. The formation of these eight products is explained in terms of the propagation sequence occurring via two resonance-stabilised allyl radicals (Scheme 7.2). Recent studies have shown that the 8- and 11-hydroperoxides are each formed in  $\sim 27\%$  yield with *cis* and *trans* isomers at about equal level and the 9- and 10-hydroperoxides are each formed in 23% yield and are almost entirely *trans* isomers. These figures require some refinement of the classical mechanism outlined in Scheme 7.2.



SCHEME 7.2. Autoxidation of methyl oleate.

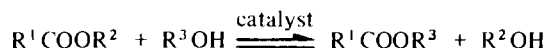
Methyl linoleate reacts 10–40 times quicker than oleate because of the enhanced reactivity of the C-11 methylene group lying between the double bonds. The reaction product is a mixture of 9- and 13-hydroperoxyoctadecadienoates and there is no firm evidence for the formation of the 11-

# CHAPTER 17

## Interesterification\*

### A. INTRODUCTION

To prepare fatty acid esters it is not necessary to start with a fatty acid and an alcohol. For example, if a triglyceride ( $R^1COOR^2$ ) is heated with an alcohol ( $R^3OH$ ), the following reaction takes place:



If  $R^3OH$  is methanol, methyl esters of the fatty acids are made. If  $R^3OH$  is glycerine, an equilibrium mixture of mono- and diglycerides is made. This is called “*alcoholysis*”.

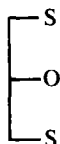
If a triglyceride ( $R^1COOR^2$ ) is reacted with a carboxylic acid ( $R^3COOH$ ), the reaction is:



In this way a  $C_{12}$  acid can be made to replace  $C_{16}$  and  $C_{18}$  acids in the triglycerides. This is called “*acidolysis*”.

In “*interesterification*” a natural oil or fat has its acyl groups randomly distributed in the glycerides, changing the physical properties depending upon how far the original oil or fat varied from a random distribution initially.

This treatment is important because the properties of a fat or oil depend not only on the fatty acid composition but also on the distribution of the fatty acids in the glycerides. For example, cocoa butter confectionery uses are attributed to the fact that it contains mainly glycerides with an unsaturated acid in position 2 and two saturated acids in positions 1 and 3, *viz.*



where S is a saturated and O an unsaturated acid. After interesterification there is random distribution of the fatty acids so that only about 12.5 % of the cocoa butter glycerides exist in the original structure and the physical properties are changed completely. Similarly, as mentioned in

\*See also Chapter 9.

Chapter 9, interesterifying soybean oil raises the melting point from  $-7$  to  $+6^{\circ}\text{C}$  and that of cottonseed oil from  $10$  to  $34^{\circ}\text{C}$ , despite no change in fatty acid composition.

On a practical basis, interesterification affords a method for changing the existing (non-random) glyceride structure of a fat to that produced by a random distribution of the fatty acids among the glycerides. Also, fatty acids may be added to a fat by interesterifying with another fat. The method can be used effectively to produce tailor-made fats and margarine oils. Since about 1950 interesterification processing has been used to such an extent that in Europe it is said to be employed as frequently as hydrogenation in many areas. In the United States major utilisation has been in the treatment of lard.

## B. TYPES OF INTERESTERIFICATION

### 1. Random

In random interesterification treatment of an oil or fat with an interesterification catalyst converts the mass into glycerides in which the fatty acids present are randomly distributed. For example: An equimolar mixture of saturated (S) and unsaturated (U) fatty acids present only as trisaturated glycerides ( $\text{GS}_3$ ) and triunsaturated glycerides ( $\text{GU}_3$ ) can be interesterified to yield  $\text{GS}_3$  (12.5%),  $\text{GU}_3$  (12.5%),  $\text{GS}_2\text{U}$  (37.5%), and  $\text{GUS}_2$  (37.5%). The amounts of the various glycerides can be calculated as follows:

$$\begin{aligned}\% \text{ triglyceride } \text{GS}_3 &= \frac{\text{S} \times \text{S} \times \text{S}}{10,000} \\ \text{GU}_3 &= \frac{\text{U} \times \text{U} \times \text{U}}{10,000} \\ \text{GSU}_2 &= 3 \left( \frac{\text{S} \times \text{U} \times \text{U}}{10,000} \right) \\ \text{GS}_2\text{U} &= 3 \left( \frac{\text{S} \times \text{S} \times \text{U}}{10,000} \right)\end{aligned}$$

where S and U are the molar percentages of saturated and unsaturated acids, respectively.

### 2. Directed

In this type of interesterification some of the fatty acids or their glycerides are removed from the equilibrium reaction, forcing it to continue to a new equilibrium. In one method, low molecular weight fatty acids are distilled out of the mixture. More commonly, the reaction is run at a low temperature such that the higher melting glycerides formed by the reaction crystallise out forcing the reaction to proceed in that direction.

## C. CATALYSTS

The most common catalysts are sodium methylate, sodium metal, or a liquid sodium-potassium alloy. It is essential that the fat contain no substances which might destroy the catalyst. This means

that the fat must be well refined, dried, and heated to about 150°C (302°F) under an inert atmosphere before the catalyst is added. Analytically, moisture below 0.01 %, free fatty acids below 0.05 %, and low peroxide value are guidelines.

### D. PROCEDURE

In random interesterification the fat is heated to about 80°C (176°F) in the presence of a catalyst (0.05–0.20 %) and with good agitation. Reaction time is about  $\frac{1}{2}$  hr. At the end of the reaction, the catalyst is inactivated with water or dilute acid.

In directed interesterification at low temperatures (26–38°C, 80–100°F), the reaction is much slower, due to the lower temperature; and for this reason, reaction time may be several hours to a day or possibly more. A solvent may also be employed to facilitate crystallisation of the rearranged more saturated glycerides. It is essential that the catalyst be inactivated with water or dilute acid before the fat is recovered in order to avoid disturbance of the equilibrium.

Some loss is always encountered because of the alkaline nature of the catalyst. This normally amounts to about 1 % neutral fat for each additional 0.1 % catalyst used over an optimum of about 0.1 %.

### E. EXAMPLES

1. A solid fat containing about 60 % essential fatty acids can be obtained by directed interesterification of sunflower oil and blending with 5 % hard fat.

2. Random interesterification of lard results in an improved shortening by reducing the graininess of the original fat, caused by the presence of large crystals of disaturated glycerides (stearic, palmitic, oleic) in which the palmitic acid is in the 2(middle)-position and the oleic in the 1-position. Random interesterification reduces the amount of these glycerides.

3. A palm oil of m.p. = 51°C containing 30 % S<sub>3</sub> and 26 % U<sub>3</sub> can be made by directed interesterification of palm oil of m.p. = 39°C containing 7 % S<sub>3</sub> and 6 % U<sub>3</sub>. Fractionation permits a higher yield of liquid oil than from the untreated oil.

4. Margarine oil made with a high content of lauric oils is typically low in melting point and has a short plastic range. This produces a margarine that is hard in the refrigerator but melts partly at room temperature. The remedy is to remove or decrease the amount of lauric triglycerides. This is done by interesterifying the coconut oil with an oil such as palm and then blending 60 % of the interesterified mixture with 40 % of an oil like sunflower.

5. A high essential fatty acid low *trans* acid margarine can be made by interesterifying a coconut-soy hardstock and blending with soybean oil. The more soybean oil in the interesterification mixture the lower the melting point, assuming the same total soybean oil in the final product.

### GENERAL REFERENCES

- HUSTEDT, H. H., "Intesterification of Edible Oils", *J. Amer. Oil Chemists' Soc.* 1976, **53**, 390.  
SCREENIVASAR, B., "Intesterification of Fats", *J. Amer. Oil Chemists' Soc.* 1978, **56**, 796.