Consumer Chemistry Unit

Additional notes: Antioxidants

Oxidation of foodstuffs

A healthy, balanced diet should contain a proportion of unsaturated and poly-unsaturated oils and fats.

These unsaturated oils and fats are, however, highly susceptible to reactions across the reactive carbon-to-carbon double bond. Oxidation reactions involving oxygen molecules from the air damage the structure of the fat (Figure 1), causing degradation of long fatty-acid chains and formation of short-chain oxidation products. The oxidation of unsaturated oils and fats primarily takes place via a free-radical-mediated process and can lead to rancidity (*rancidus* [Latin] = stinking), which negatively affects both odour and taste, and has an impact on safety for human consumption.

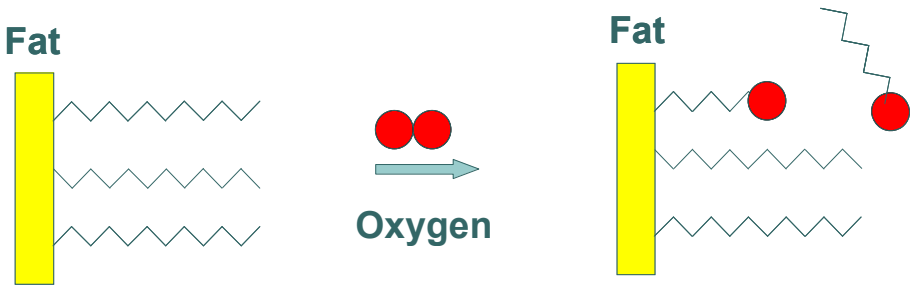


Figure 1: Oxidation damages the structure of fats and oils.

Reducing the rate of oxidation of foodstuffs

The rate of oxidation of foodstuffs can be slowed down by reducing the temperature by refrigeration. Packaging under a vacuum or under an inert gas such as nitrogen can also reduce the oxidation rate by reducing the concentration of oxygen (air). Crisp manufacturers fry potatoes under a blanket of steam to reduce the oxygen concentration, thus extending the lifetime of both the frying oil and of the crisps.

Although all of these methods of reducing oxidation are fairly effective, it is still usual to add antioxidant(s) to foodstuffs to prolong their shelf-life.

Antioxidants

Antioxidants are molecules that reduce the rate of oxidation reactions involving the transfer of electron(s) to an oxidising agent. Antioxidants are often added to foodstuffs to minimise oxidative damage.

An effective classroom demonstration to illustrate the benefits of antioxidants in foodstuffs involves cutting an apple in half and leaving one side exposed to the oxygen in the air. The other side is coated in lemon juice, which contains a high concentration of the antioxidant vitamin C. After a few hours, the untreated half becomes brown due to free-radical-induced oxidative damage, whereas the treated half remains undamaged due to the antioxidant properties of the vitamin C.

Free radicals

Oxidation reactions can produce **free radicals**. Free radicals are highly reactive species containing an unpaired electron in their outer shell. A free radical will remove an electron from another atom/molecule in order to become stable. This leaves the second atom/molecule an electron short, and so it in turn removes an electron from a further atom/molecule in order to achieve stability. Hence, formation of free radicals often results in a **chain reaction**.

Most free radicals contain oxygen atoms, and they are sometimes referred to as 'reactive oxygen species'. Examples include the superoxide ion (O_2^-) and the hydroxyl radical ($^{\cdot}OH$).

Free radicals 'steal' electrons from fatty foods, resulting in the structural damage and eventual rancidity described above. This oxidative process proceeds via a free radical chain reaction mechanism (Figure 2). Polyunsaturated oils and fats are particularly badly affected by free radical oxidation since they contain multiple double bonds.

The free radical chain reaction in the oxidation of fats

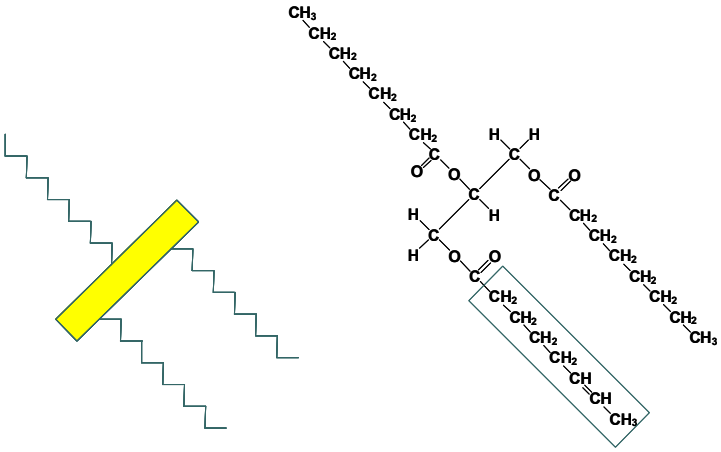
A free radical chain reaction consists of three main steps: **initiation**, **propagation** and **termination**.

In the **initiation** step, highly reactive free radicals are formed when a reactive oxygen species (eg a hydroxyl radical) abstracts a hydrogen atom from a carbon atom close to the double bond in the unsaturated fat molecule.

In the **propagation** step, new reactive free radicals are formed as the original free radicals react to become stable.

In the **termination** step, two free radicals combine and cancel each other out to form stable oxidation products. These stable oxidation products are the cause of the typical rancid odour of oxidised foods.

These steps are illustrated diagrammatically in Figure 2 for an unsaturated fat molecule.



Unsaturated fat

$R\text{-}CH_2CH_2CH_2CH_2CH_2CH{=}CH_3$

Note: 'R' represents the remainder of the triglyceride molecule

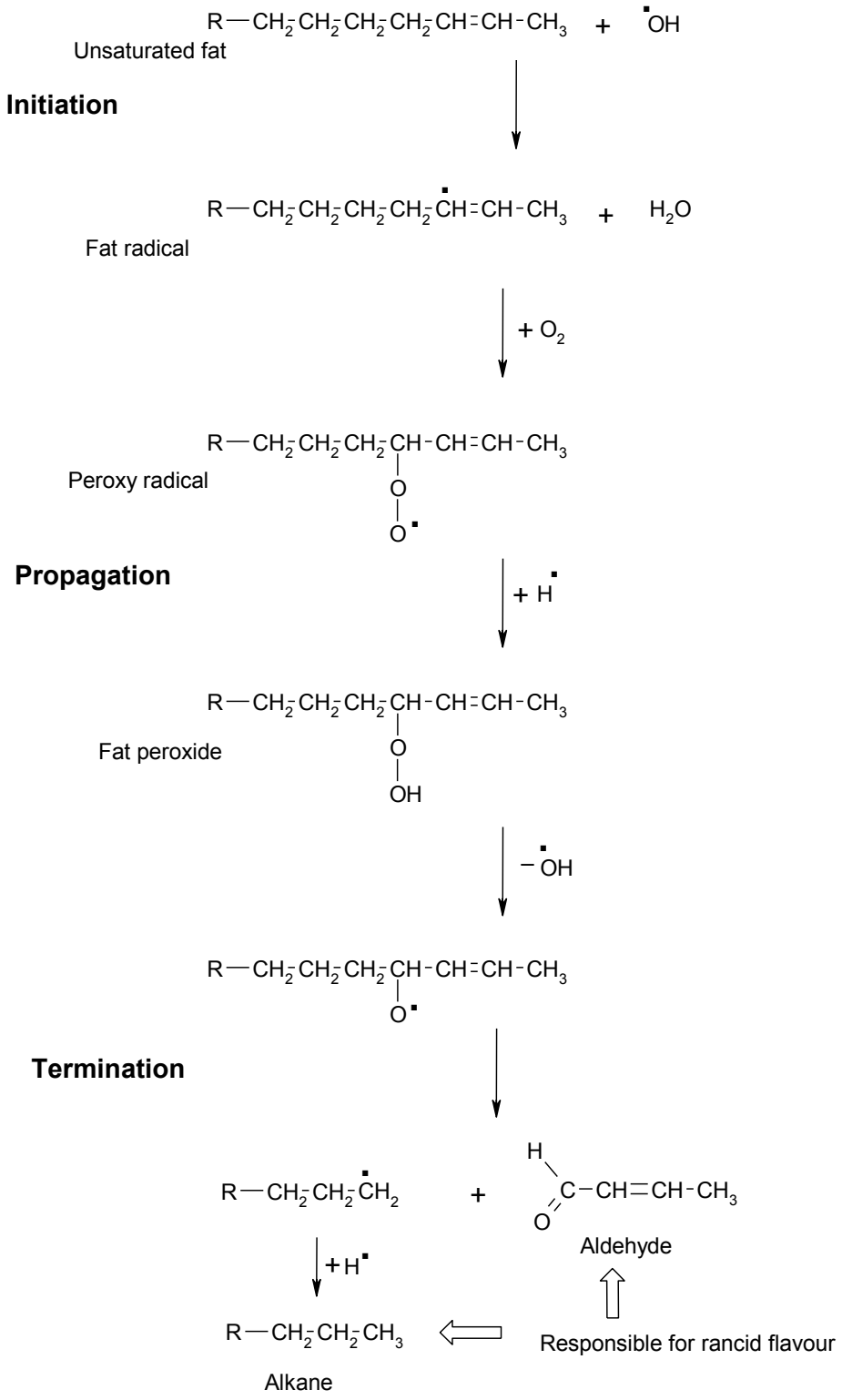


Figure 2: Free radical chain reaction in an unsaturated fat.

Antioxidants 'deactivate' the free radicals formed during the oxidation process by becoming oxidised themselves and therefore inhibiting the formation of further free radicals. Antioxidants can terminate the chain reaction at the initiation step or can interrupt the propagation step.

Natural and synthetic antioxidants

Antioxidants can be natural or synthetic. Natural antioxidants tend to be short-lived and therefore synthetic antioxidants are used when a longer shelf-life is preferred. In reality, several antioxidants are often added in combination to foodstuffs to give the most effective action.

Natural antioxidants added to food include vitamin C (ascorbic acid), vitamin E (tocopherols), flavonoids (eg flavone) and polyphenols (eg apigenin), as shown in Figure 3.

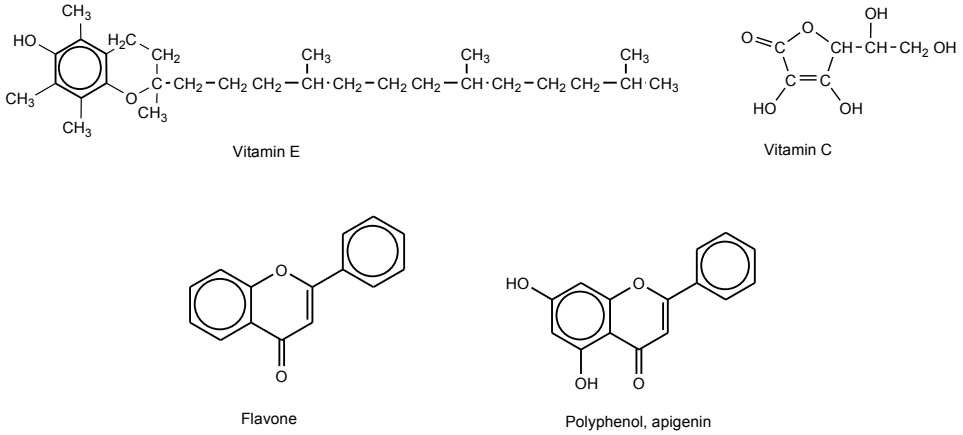
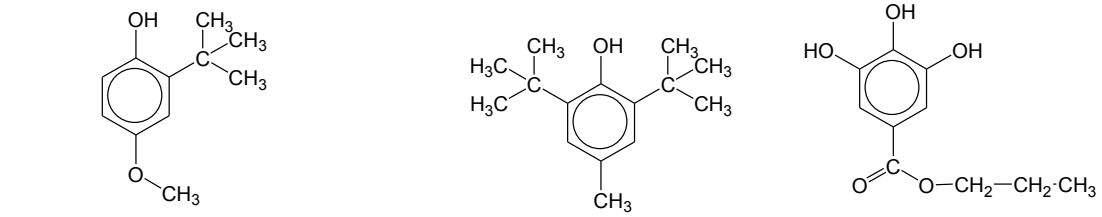


Figure 3: Natural antioxidants.

Vitamin C and its salts are added to soft drinks, jams, condensed milk and sausage to prevent oxidation. The tocopherols are members of the vitamin E family and are found mainly in nuts, sunflower seeds, soya and maize shoots. They are mostly used for preserving vegetable oils, margarine and cocoa products.

Ascorbic acid and tocopherols are also produced synthetically, as the demand for these popular antioxidants cannot be met from natural sources alone. Synthetic antioxidants include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and propyl gallate, which are shown in Figure 4. The most important synthetic antioxidants belong to the family of gallates. Gallates are added mostly to vegetable oils and margarine to prevent rancidity and preserve taste.



butylated hydroxyanisole (BHA) butylated hydroxytoluene (BHT) propyl gallate

Figure 4: Synthetic antioxidants.

One important antioxidant property of vitamin C is its ability to behave as a reducing agent (electron donor), as shown in Equation 1.

$C_6H_8O_6$	$\rightarrow$	$C_6H_6O_6 + 2H^+ + 2e^-$	Equation 1
Vitamin C		DHA	
(ascorbic acid)		(dehydroascorbic acid)	

Vitamin C gives little protection to fatty foods because of its high water solubility and low solubility in fat, therefore the fat-soluble ester derivatives of vitamin C (the ascorbates) are added to protect fatty foods against oxidation.

Most antioxidants contain conjugated systems of double bonds arranged in either linear chains or aromatic systems. When a free radical comes along, the antioxidant molecule will readily give up an electron (become oxidised) to save the food from further damage. The newly formed radical on the antioxidant molecule is much less reactive because the radical charge is able to delocalise throughout the system of conjugated double bonds. This process can be illustrated through the example of the synthetic antioxidant BHA (Figure 5).

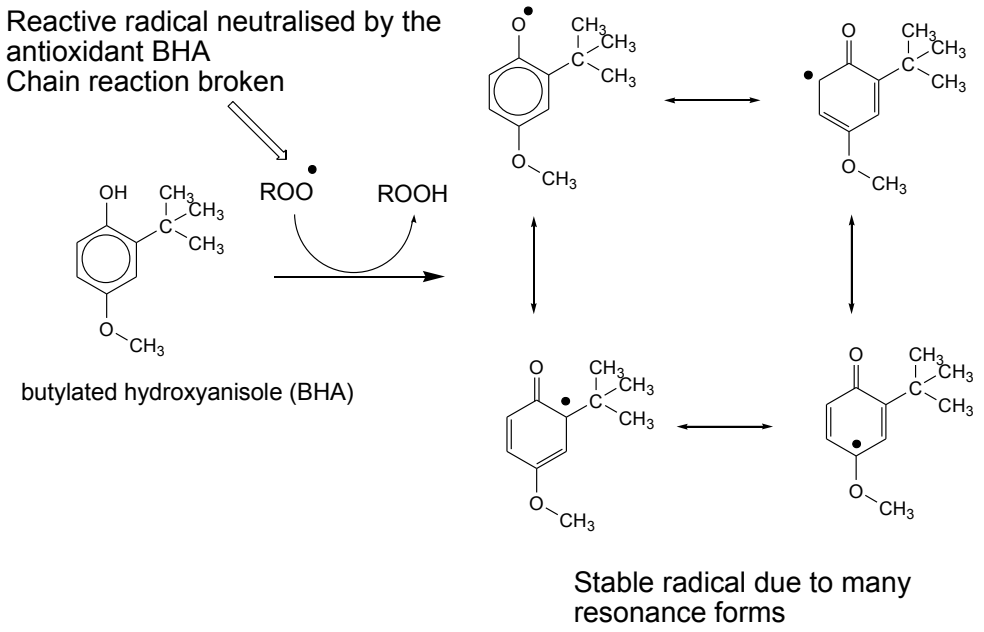


Figure 5: Synthetic antioxidant BHA terminating a chain reaction.

Antioxidants in fruit and vegetables

Although the body can produce some of the antioxidants it requires, more need to be obtained from the diet. Many fresh foods are natural sources of antioxidants (Table 1).

Without antioxidants the body would become vulnerable to illness and/or disease. Claims by scientists suggest that foods rich in antioxidants can help to protect against ageing, cancer, heart disease and strokes. This has prompted many food manufacturers to market products rich in antioxidants as 'superfoods' that will be beneficial to health. Examples of 'superfoods' rich in antioxidants include cranberries, pomegranate, blueberries, broccoli, olive oil, apples and tea.

Table 1: Foods rich in antioxidants

Antioxidant compound	E number	Examples of foods containing high levels of these antioxidants
Vitamin C (ascorbic acid)	E300	Fruit drinks, jams, strawberries, tomato soup, red peppers
Vitamin E (tocopherols)	E306-309	Vegetable oils, almonds, spinach, olives
Polyphenols (flavonoids)		Tea, coffee, soy, fruit, olive oil, chocolate, cinnamon, oregano, red wine
Propyl gallate Octyl gallate	E310 E311	Frying oils and fats, seasoning, dehydrated soups, chewing-gum
Butyl hydroxyanisole (BHA) Butyl hydroxytoluene (BHT)	E320 E321	Sweets, raisins, processed cheese, peanut butter, instant soups