A Kinetic Study on the Autoxidation of Sunflowerseed Oil

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ABSTRACT: Unhydrogenated and hydrogenated sunflowerseed oils were exposed to the autoxidation process by sunlight under atmospheric conditions. Experiments were carried out in equal-sized glass, PET (polyethylene terephthalate) polymer, and metal (covered by tin) containers. The reaction time was 30 d, and the reaction course was observed by determining weight changes and peroxide values (PV) of the oil samples at the same time within 2-d intervals. The logarithm of the PV was plotted against time, and straight lines were obtained from the 4th or 6th d. The autoxidation reaction constants were obtained for each oil in each container. When comparing the reaction constants, the unhydrogenated oils autoxidize easily, and the autoxidation reaction occurs faster in sunlight in glass than in the PET polymer container and much faster than in the darkness of the metal container.

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KEY WORDS: Autoxidation, kinetics, mechanism, peroxide value, reaction rate, sunflowerseed oil, weight change.

Previous reviews (1–3) covered studies from early workers in lipid oxidation. Farmer and his group at the British Rubber Producers' Research Association (4–7) developed the generally accepted free-radical mechanism of autoxidation that involves attack of oxygen at the allylic position with formation of unsaturated hydroperoxides (HP).

Other pioneers in this field and their major contributions include Privett and coworkers at the Hormel Institute (8,9) who described the autoxidation mechanism and kinetics of unsaturated fatty acids.

Oxygen reacts with many organic substrates (RH) to yield HP and other oxygenated compounds. This oxidation is in most instances a free-radical chain reaction that can be described in terms of initiation, propagation, and termination processes (Reactions 1–5) (10,11).

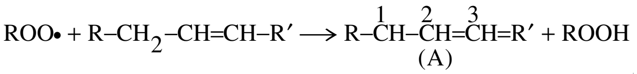
$$\text{Initiation: } RH \xrightarrow{\text{Initiator}} R\bullet \qquad [1]$$

This production of free radicals may take place by direct thermal dissociation (thermolysis), by HP decomposition, by metal catalysis, and by exposure to light with or without the intervention of photosensitizers.

$$\text{Propagation: } R\bullet\ O_2 \longleftrightarrow ROO\bullet \qquad [2]$$

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet \qquad [3]$$

The susceptibility of RH to autoxidation depends on their relative ease to donate a hydrogen by Reaction 3. With unsaturated fats, susceptibility to autoxidation depends on the availability of allylic hydrogens for reactions with peroxy radicals.

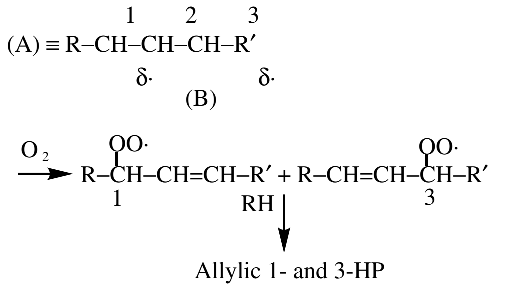


$$ROO\bullet + R\text{–}CH_2\text{–}CH{=}CH\text{–}R' \longrightarrow R\text{–}\overset{1}{C}H\text{–}\overset{2}{C}H{=}\overset{3}{C}H{=}R' + ROOH$$

(A)

[4]

Valence bond structure (A) may be represented as a hybrid (B) with a partial free radical at each end of the allylic system. Reaction of oxygen occurs at end carbon positions of the allylic system to produce a mixture of isomeric HP:



$$\text{Termination: } ROO\bullet + ROO\bullet \rightarrow \text{nonradical products} \qquad [5]$$

The most important termination process for secondary peroxy radicals at room temperature is that proposed by Russel (12) and involves a tetraoxide intermediate to produce a ketone, an alcohol, and oxygen (Reaction 6).

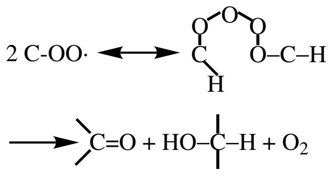


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TABLE 1
Fatty Acid Compositions (wt%) of Unhydrogenated and Hydrogenated Sunflowerseed Oils

Fatty acid	Unhydrogenated	Hydrogenated
Myristic, $C_{14:0}$	0.1	0.1
Palmitic, $C_{16:0}$	7.7	8.5
Stearic, $C_{18:0}$	3.6	5.1
Oleic, $C_{18:1}$	24.7	76.6
Linoleic, $C_{18:2}$	63.9	9.7

Because sunflowerseed oil is mostly composed of oleic and linoleic acids as shown in Table 1, we will only deal with the autoxidation mechanisms of these fatty acids. According to the most accepted mechanism of oleate autoxidation (13), hydrogen abstraction from the allylic methylenes on carbon-8 and carbon-11 produces two allylic radicals in which electrons are delocalized through 3-carbon systems. However, these four isomeric HP would be formed in equal amounts.

These allylic radicals react with O_2 at the end positions to produce a mixture of 8-, 9-, 10-, and 11-HP isomers (Scheme 1).

The mechanism of linoleate autoxidation proceeds by hydrogen abstraction from the doubly allylic methylene on carbon-11 to produce a delocalized pentadienyl radical (13). Oxygen attack at the end positions produces an equal mixture of conjugated 9- and 13-HP isomers with *trans, cis*-configuration (Scheme 2).

The aim of this work was to perform a kinetic study by gravimetric monitoring and by determining the peroxide values (PV) for the autoxidation of unhydrogenated and hydrogenated sunflowerseed oil samples.

EXPERIMENTAL PROCEDURES

Materials. An analytical VA 304 balance (Gec Avery Limited, Birmingham, England) with precision of ±0.1 mg was used. All chemicals used were of analytical grade.

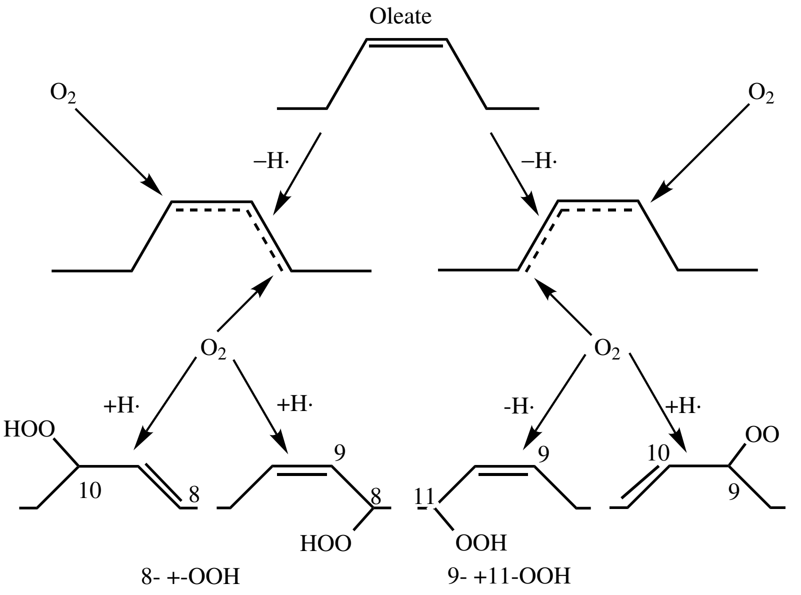
Two types of sunflowerseed oil were used. One was unhydrogenated oil [PV = 0.6 and iodine value (IV) = 131.7], and the other was hydrogenated oil (PV = 8.3 and IV = 82.4). These oils were supplied by the Thrace Union (Trakya Birlik) Co. (Edirne, Turkey).

Hydrogenation was carried out under the following conditions: catalyst concentration, 0.02% as Ni; temperature, 180°C; pressure, 2 atm H_2; agitation, 450 rpm; and reaction time, 25 min.

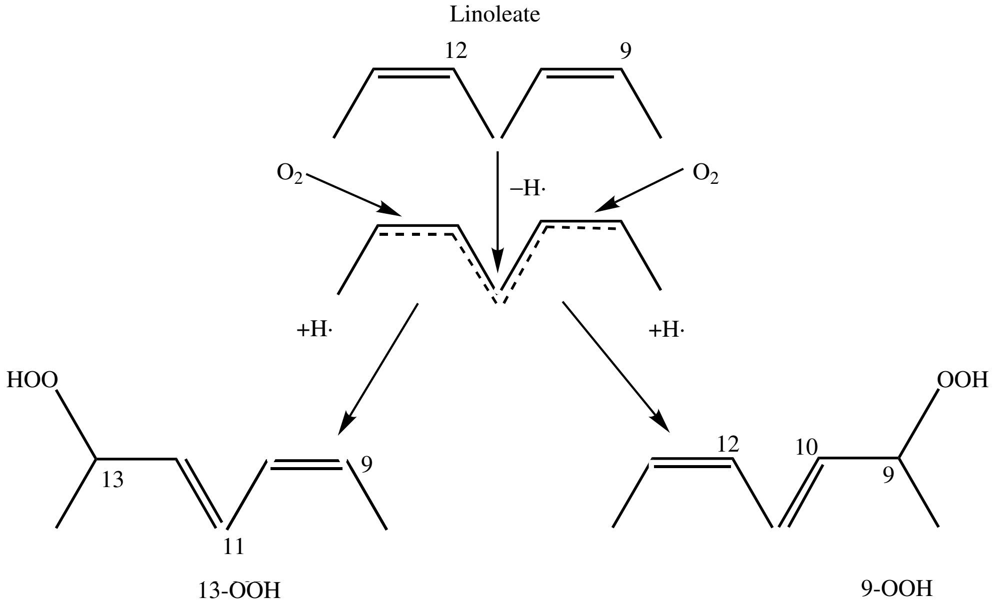
For analysis of the fatty acid composition, a Shimadzu GC 6 AM Model gas chromatograph was used (Shimadzu, Kyoto, Japan). The type of gas-chromatographic column was 2 m × 1/4″ × 2 mm glass, packed with 5% PEGA on chromosorb W 60–80 mesh, and its conditions were: injector temperature, 225°C; detector temperature, 225°C; column temperature, 175°C; gas pressure, air, 1 kg cm^{-2}; gas pressure, H_2, 3 kg cm^{-2}; carrier gas pressure, 5 kg cm^{-2}; and sample quantity, 1 µL of 3% solution in hexane.

Determination of PV. The American Oil Chemists' Society method (14) was used, the principle of which is as follows. The sample, dissolved into an acetic acid/chloroform mixture (3:2, vol/vol), was mixed with 0.5 mL of a standard solution of potassium iodide. The released iodine was titrated with a standard solution (0.01 N) of sodium thiosulfate after manual shaking for 1 min and resting in the dark for 5 min.

Determination of IV. For this purpose, the Wijs method



SCHEME 1



SCHEME 2

(15) was used. The principle of this method is as follows. The sample is treated with iodine monochloride (ICl) solution. After addition of the halogen, the excess of ICl is titrated with sodium thiosulfate (0.1 N) solution.

Gravimetric monitoring of autoxidation of sunflowerseed oils. Samples were poured into equal-sized glass, PET (polyethylene terephthalate) polymer, and metal containers (covered by tin) of 3-cm internal diameter after weighing. They were weighed at the same time after 2-d intervals.

Autoxidation procedure. Unhydrogenated and hydrogenated sunflowerseed oil samples were exposed directly to sunlight and air oxygen outdoors under atmospheric conditions. One sample was taken for each PV determination and poured into 15 identical containers for each kind of container and oil at time zero. The containers were quite open. The autoxidation time was 30 d. All experiments were carried out during sunny days in August.

RESULTS AND DISCUSSION

First, the autoxidation rate was studied from the weight changes by using identical containers (Figs. 1 and 2). The parameter used for gravimetric monitoring was the percentage gain, W, which is given by Equation 1:

$$W = \frac{W_t - W_0}{W_0} 100 \qquad [1]$$

where W_t and W_0 are the weights at a given time t and at time zero, respectively. The weighing method gives a sum of the dissolved and not yet reacted O_2 and the O_2 reacted to HP. For the glass and PET containers and the unhydrogenated sunflowerseed oil, plotting of the values in Figure 1 according to natural logarithm (ln) (100 × wt%) against time t gave a straight line after about 10 d for the glass container, 16 d for the PET container, and 20 d for the metal container to the end at 30 d (Fig. 3).

When the autoxidation rate has reached a high enough value, the O_2 level of the HP dominates the weight change. And also, as remarked above for the PV measurements, the kinetics of the autoxidation is different during the first few days. According to the weighing method, the values of the autoxidation rate constant k_w for unhydrogenated sunflowerseed

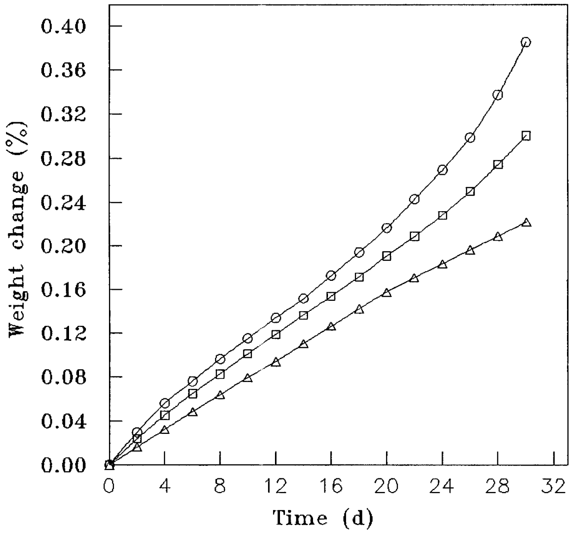


FIG. 1. Weight changes of unhydrogenated sunflowerseed oil against time: ○, in glass container; □, in polyethylene terephthalate (PET) container; and △, in metal container.

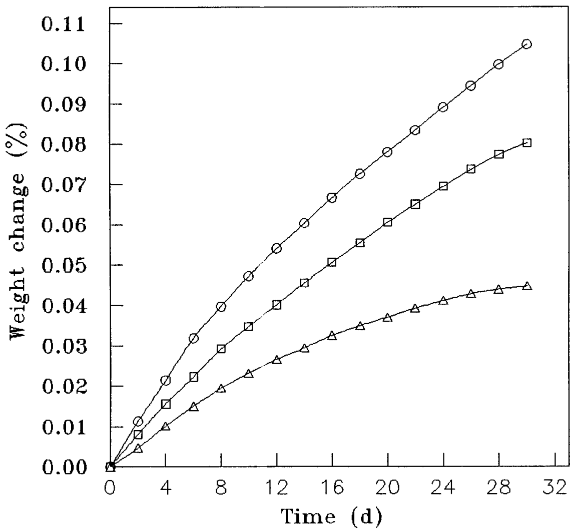


FIG. 2. Weight changes of hydrogenated sunflowerseed oil against time: ○ in glass container; □, in PET container; and △, in metal container. See Figure 1 for abbreviation.

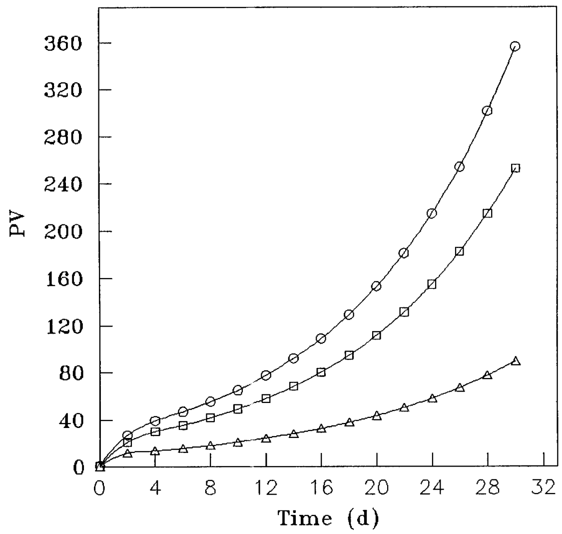


FIG. 4. Peroxide value (PV) changes of unhydrogenated sunflowerseed oil against time: ○, in glass container; □, in PET container; and △, in metal container. See Figure 1 for other abbreviation.

oil were 5.9 × 10^{-2} wt/d in the glass container for 10–30 d; 4.7 × 10^{-2} wt/d in the PET container for 16–30 d; and 3.4 × 10^{-2} wt/day in the metal container for 20–30 d.

The kinetic curves obtained from all these values showed that the unhydrogenated oil gained more weight than hydrogenated oil, and the weight gain of the oil samples in the glass container was greater than for the others (PET and metal containers).

Figures 4 and 5 show the changes in the PV. The PV values increase continuously with time. The PV increments for unhydrogenated oil are larger than for hydrogenated oil because unhydrogenated oil has more unsaturation than hydrogenated. A measure of the unsaturation is the IV. Because the IV of unhydrogenated oil is 131.7 and it is 82.4 for hydrogenated, unhydrogenated oil has more unsaturation. The curves in Figures 4 and 5 and the lines in Figures 6 and 7 show that the exponential increase of the PV does not start until after 2–4 d. Not until the amount of HP has reached the critical micelle concentration of HP in the oil does O_2 begin to solubilize into oil (16). Then the amount of HP increases exponentially as does the PV.

Because the accelerated formation of HP molecules starts

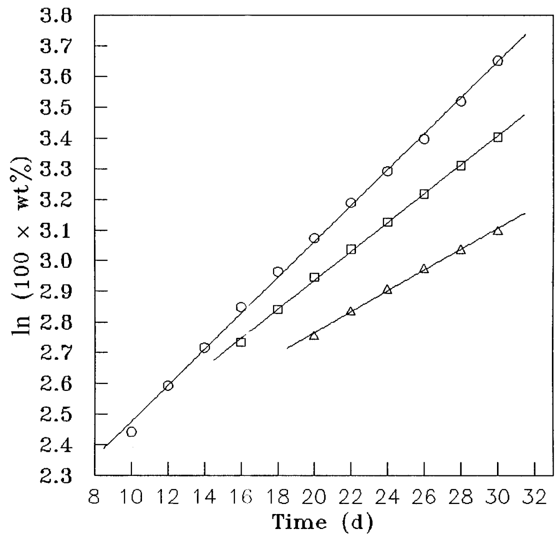


FIG. 3. Plot of natural logarithm (ln) (100 × wt%) vs. time for unhydrogenated sunflowerseed oil: ○, in glass container; □, in PET container; and △, in metal container. See Figure 1 for other abbreviation.

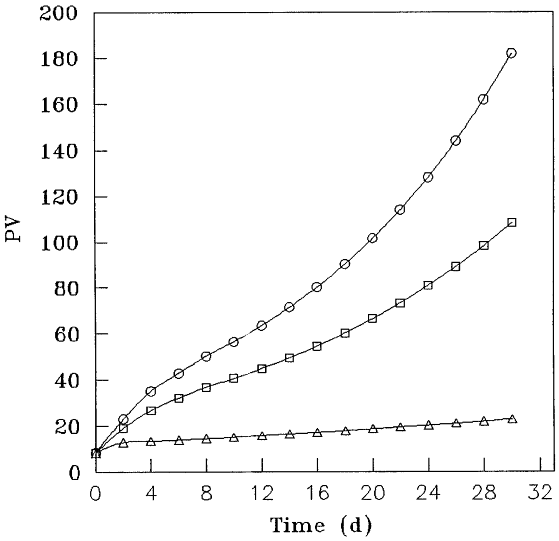


FIG. 5. PV changes of hydrogenated sunflowerseed oil against time: ○, in glass container; □, in PET container; and △, in metal container. See Figures 1 and 4 for abbreviations.

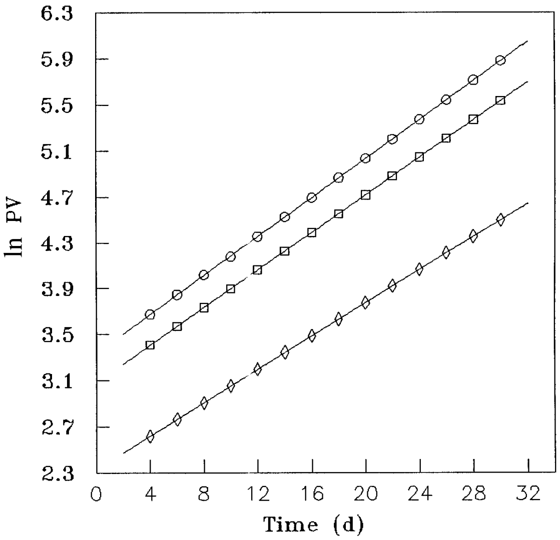


FIG. 6. Plot of ln PV vs. time for unhydrogenated sunflowerseed oil: ○, in glass container; □, in PET container; and △, in metal container. See Figures 1, 3, and 4 for abbreviations.

after the fourth day, the autoxidation reaction course depends on the concentration of HP. Therefore, the reaction rate, r, is as illustrated in Equation 2:

$$r = \frac{d[\mathrm{HP}]}{dt} = k_{\mathrm{PV}}\,[\mathrm{HP}] \text{ or } r = \frac{d\mathrm{PV}}{dt} = k_{\mathrm{PV}}\,\mathrm{PV} \qquad [2]$$

To calculate the autoxidation reaction constant, k_{PV}, we considered the PV values of 4–30 d, and then we plotted *ln* PV vs. time t (Figs. 6 and 7). According to the PV measurements, the values of k_{PV} for unhydrogenated oil were 8.5×10^{-2} PV/day in the glass container; 8.2×10^{-2} PV/day in the PET container; and 7.2×10^{-2} PV/day in the metal container.

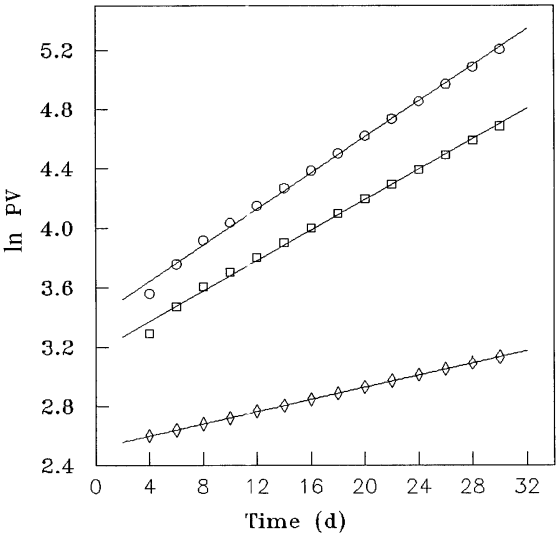


FIG. 7. Plot of ln PV vs. time for unhydrogenated sunflowerseed oil: ○, in glass container; □, in PET container; and △, in metal container. See Figures 1, 3, and 4 for abbreviations.

The values of k_{PV} related to hydrogenated oil were 6.1×10^{-2} PV/day in the glass container; 5.1×10^{-2} PV/day in the PET container; and 2.0×10^{-2} PV/day in the metal container.

Depending on the values of k_{PV} and k_{W}, first we can say that unhydrogenated oil will autoxidize fast, compared to hydrogenated oil, and the autoxidation reaction in the glass container is faster than in the PET and metal containers. As a result of this study, we advocate that especially the unhydrogenated oils, which may undergo fast and easy autoxidation, must be kept in containers that do not get into contact with sunlight and air oxygen. Therefore, one must prefer containers that have an inert surface and no light transmittance for long-term preservation of oils.

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