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Abstract

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ON THE NATURE OF THE INDUCTION PERIOD OF THE AUTOOXIDATION OF FATS AND FATTY ACIDS

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It is known that the initial reaction in the autooxidation of fats and fatty acids is the addition of molecular oxygen to the oxidized substance, with the formation of peroxides (hydroperoxides), which serve as the starting compounds for the subsequent autocatalytic chain mechanism of the entire autooxidation process:

$$RH + O_2 \rightarrow ROOH;$$

$$ROOH + ROOH \rightarrow R^{\cdot} + ROO^{\cdot} + H_2O;$$

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot};$$

$$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}.$$

Indeed, in many cases of the autooxidation of natural fats and fatty acids, at the beginning of the process only a very slight increase in rate is observed. The interval between the start of contact of the oxidized substance with oxygen and the moment when a sufficiently high rate of the oxidative process is reached is called the induction period, since this term is usually associated with the concept of the initial reactions of peroxide formation, which then, upon reaching a certain concentration, autocatalytically accelerate the further oxidation process. Such a view of the nature of the induction period is widespread and is accepted by many investigators.

A number of authors, however, have been unable to detect an induction period in the oxidation of chemically pure substances ([1]). In experiments studying the absorption of oxygen by well-purified and freshly distilled oleic acid at 20–60°, we likewise did not observe an induction period ([2]). This agrees with the results of Hamilton and Olcott ([3]), who found that, in the oxidation of pure methyl oleate, no induction period occurs.

Certain investigators believe ([1]) that, especially in the case of the oxidation of fatty substances, the phenomenon of the induction period could be explained by the presence in them of impurities of natural inhibitors (HA), readily oxidized substances that terminate the chain process of autooxidation:

$$ROO^{\cdot} + HA \rightarrow ROOH + A^{\cdot}$$

or

$$R^{\cdot} + HA \rightarrow RH + A^{\cdot},$$

since $A^{\cdot}$ cannot sustain the chain reaction of autooxidation.

In our investigations it was established that the autooxidation of unsaturated fatty acids and fats that do not contain natural oxidation inhibitors proceeds, in the temperature range from 40 to 60°, without an induction period. At the same time, already in the very initial stages of the process, in addition to peroxide formation, a rapid accumulation of oxy-epoxy compounds is observed. As an example, one of our experiments on the autooxidation of pure oleic acid, which gives no Kreis reaction ([4]), at 40° may be cited; its results are given in Fig. 1. In this experiment, in the course of autooxidation

were determined: total oxygen uptake ([2]), peroxides (by Wheeler), epoxide oxygen ([5]), and oxygen of oxy groups ([6]). The results of the determinations are given in Fig. 1, in milligrams of oxygen per 1 g of oleic acid.

As is evident from Fig. 1, the uptake of molecular oxygen (curve 1), the accumulation of epoxide oxygen (curve 2), and the oxygen of OH groups (curve 3) in the autoxidation products occur without any induction period. If, however, one judges by the accumulation of peroxide oxygen (curve 4), one may arrive at the conclusion that such an induction period is present.

Fig. 1

Fig. 2

This is explained by the fact that in the initial stages of the autoxidation process, along with the formation of peroxides, there occurs, as is evident from Fig. 1, their rapid conversion into oxyepoxy compounds

$$-CH=CH-CH- \longrightarrow -\underset{\displaystyle OOH}{\underset{|}{CH}}-CH-\underset{\displaystyle OH}{\underset{|}{CH}}-$$

$$-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle O}{\underset{\diagdown\,/}{CH}}-$$

which are what accumulate in the autoxidation products. Owing to this transformation, the peroxide content in the autoxidation products remains at a comparatively low level throughout the initial stage of oxidation, and the oxygen of peroxides constitutes only an insignificant fraction of the absorbed oxygen. The main part of it is present in the autoxidation products during the primary phase of oxidation in the form of oxyepoxy compounds. Therefore one cannot judge the depth and rate of the oxidation process from the amount of peroxides formed, and such a method can lead only to the detection of a false induction period.

In the autoxidation of fats containing substances that are part of the unsaponifiable fraction (including natural inhibitors), almost the entire oxidative process at the very beginning is concentrated on these additional components of the fat. As an example of this type of autoxidation one may cite the experiment on the oxidation of refined milk fat containing carotenoids.

Fig. 2 presents the results of an experiment on the oxidation of such a fat with an iodine value of 35.6. The experiment was carried out at 70° in air and in the complete absence of light. In the course of autoxidation the following were determined: carotenoids (photometrically), iodine values by Rosenmund and Kuhnhenn ([7]), peroxides (by Wheeler), epoxide oxygen ([5]), and oxygen of oxy groups ([6]). The results of the determinations are expressed as follows: carotenoids (curve 1) in gammas of carotene per 1 g of fat; oxygen of OH groups (curve 3), epoxide groups (curve 4), and peroxides (curve 5)—in milligrams of oxygen per 1 g of fat; and the decrease in iodine values (curve 2) as the difference.

From the data of this experiment it is evident that from the beginning of the process and for 100 hours the triglycerides of the fat are oxidized only slightly, because the carotenoids of the fat undergo vigorous oxidation. Only after the oxidation of the carotenoids approaches its final phase is a sharp increase observed in the rate of oxidation of the triglycerides. Thus, the observed "induction period" is due to the fact that at first vigorous oxidation of the carotenoids takes place, which protects the triglycerides from oxidation in the early stages. In this case the term "induction," naturally, loses its meaning, since the initial inhibition of triglyceride oxidation in the present case has an entirely different nature.

Analogous results were also obtained in experiments on the autoxidation of other natural fats containing carotenoids, for example beef fat, and also in the oxidation of mixtures of triglycerides of natural fat and carotenes. All these results show that in a number of cases of oxidation of triglycerides of natural fats, the observed induction period is caused by the oxidation of readily oxidized substances of the unsaponifiable fraction present in the fat. In addition, from the data obtained in the indicated autoxidation experiments, it is clear that in studies limited to observations of the formation of any one product of autoxidation, for example peroxides, a false induction period may be detected. Therefore it is necessary not only to determine oxygen absorption and to determine other products of autoxidation, but also to study the oxidation of all the main com-

ponents of the complex system of natural fat, including the substances of the unsaponifiable fraction.

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Note: Figure translations are in progress. See original paper for figures.