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# Study of Thermal Oxidation of Thin Film of Trilinolein by Thermogravimetric Analysis

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**The thermal oxidation of thin film of trilinolein has been investigated. The amounts of thermal decomposition products and polymerization products were determined using vacuum thermogravimetric analysis (vacuum TGA). It was found that the thermal oxidation decomposition and polymerization occurred in at least the outermost 120 μ of trilinolein films heated at 200 C for 4 min. In addition, it was found that the thermal polymerization is markedly affected by the nature of sample pans.**

In recent years, the thermal oxidation reactions of oil during storage and thermal treatment have been investigated extensively, and a number of papers on the subject have been published (1-7). Although most studies have been carried out by using bulk phase rather than thin film phase of oil, studies on the thin film of oil are very limited (8-10). In addition, in the case of cooking and lubrication, the oil generally is used as a thin film phase. Therefore, the study of thermal oxidation reaction of thin film is of particular importance.

On the other hand, it is well known that the thermal oxidation reaction of oil occurs at the oil surface and is influenced by the nature of the utensil. Such surface reactions are difficult to monitor by conventional experimental methods. The suitable surface analytical techniques were not commonly available at the time these studies were carried out. Thus, we have used a modified vacuum thermogravimetrical analysis (vacuum TGA) to investigate the thermal oxidation reaction of thin film.

In this study, attempts were made to investigate the thermal oxidation decomposition and polymerization of thin film of trilinolein by vacuum TGA.

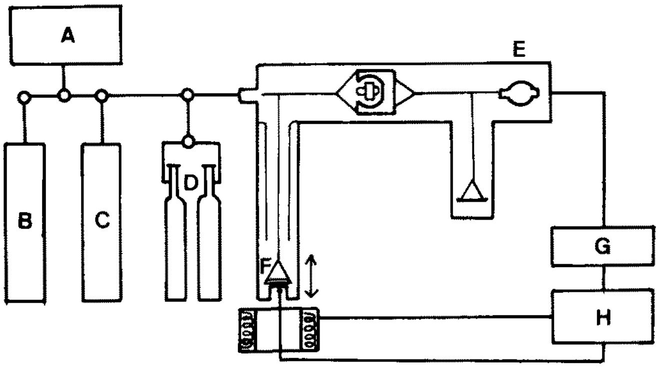

FIG. 1. Schematic diagram of appratus. A, Ionization vacuum gauge; B, rotary pump; C, diffusion pump; D, gas cylinder; E, detector; F, sample pan; G, recorder; H, thermal controller.

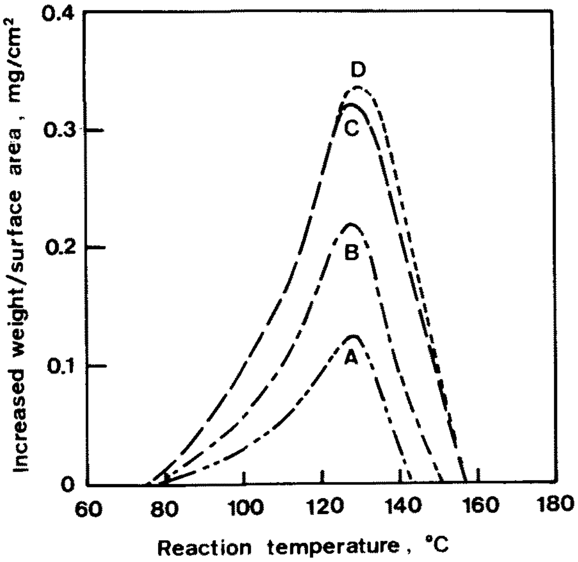

FIG. 2. Thermogravimetric curve of trilinolein in air. Film thickness: A, 90 μ; B, 230 μ; C, 410 μ; D, 780 μ.

## EXPERIMENTAL

*Materials.* 1,2,3-Tri-[(*cis,cis*)-9,12-octadecadinoyl)]-rac-glycerol(Trilinolein, purity 99%) was obtained from Sigma Chemical Co. (St. Louis, Missouri) and was used without purification.

*Apparatus.* A Shimazu TB-20 electric microthermobalance equipped with a modified chamber for measuring thermal decomposition products and thermal

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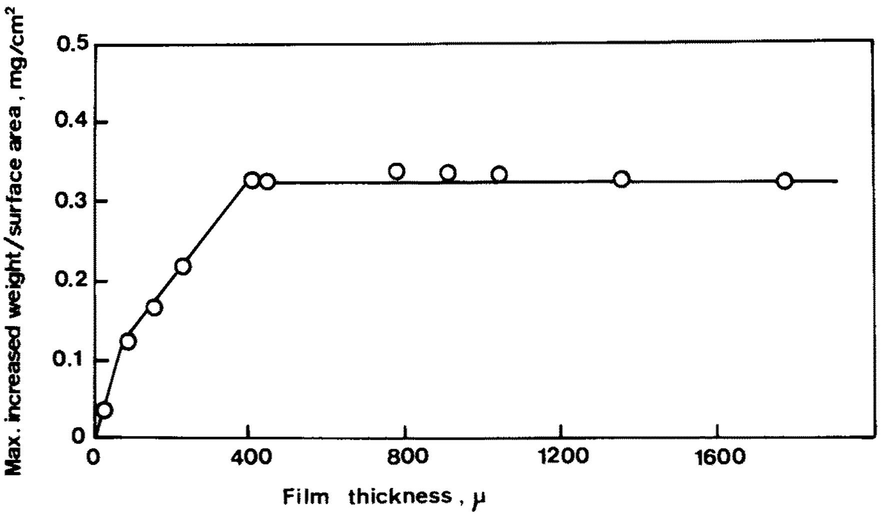

**FIG. 3. Relation between film thickness and maximum increased weight of trilinolein in air.**

oxidation polymerization products was used throughout this study. A schematic diagram of the experimental apparatus is shown in Figure 1. It is a vacuum thermogravimetric analyzer (vacuum TGA).

A thermogravimetric curve was measured using vacuum TGA apparatus in range from 25 C to 500 C and at a rate of 5 C/min. The sample pans used in this study were cleaned with dimethyl ether before use. The samples were placed in sample pans, which are made of platinum, iron and silica, respectively. After homogeneous spread of oil was confirmed, the pan was then placed in the furnace at room temperature and degassed under a reduced pressure of $1 \times 10^{-5}$ mmHg (1 mmHg = 133.332 Pa). The sample was heated at 5 C/min to 500 C. The apparatus was then cooled in preparation for the next experiment. The silica and platinum pans were wiped off and heated in the flames after each experiment. The iron pan was discarded after each experiment. The furnace was cleaned by raising the temperature to 800 C.

The film thickness was determined from amount of oil and area of pan by assuming the homogeneous spread of oil.

## RESULTS AND DISCUSSION

The trilinolein on the platinum pan was heated in air from 25 C to 170 C at a rate of 2 C/min. Figure 2 shows the relationship between increased weight per unit surface area and the reaction temperature of trilinolein in air. It can be seen from Figure 2 that the weight of the sample increases gradually from about 76 C by oxidation, reaches a maximum value at about 130 C, and decreases above about 130 C by evaporation of volatile products. The maximum increased weight was plotted against the film thickness of sample. The results are shown in Figure 3. It can be seen from Figure 3 that the maximum weight increases as the thickness of film does, reaching a plateau above 410 $\mu$ thickness. The constant value above 410 $\mu$ thickness means that only the surface layer of oil oxidizes under these conditions.

In order to investigate the amount of thermal oxidation polymerization products, the measurement of vacuum TGA was carried out. The trilinolein films of 17-170 $\mu$ thickness on silica pan were heated at 200 C for 4 min. After heating for 4 min, the furnace was quickly shut down, and the sample was rapidly cooled to room temperature by the use of a refrigerator; the weighing chamber was successively evacuated to $10^{-5}$ mmHg. The sample was then heated from 20 C to 500 C at a rate of 5 C/min, and a thermogravimetric curve under reduced pressure was obtained, as shown in Figure 4. As can be

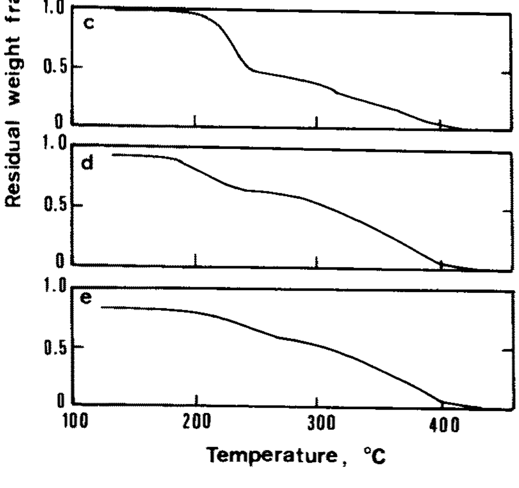

**FIG. 4. Vacuum thermogravimetric analysis of heated trilinolein at 200 C for 4 min in air. Film thickness: a, 168 $\mu$; b, 118 $\mu$; c, 84 $\mu$; d, 33 $\mu$; e, 17 $\mu$. The dotted line indicates vacuum thermogravimetric curve of unheated trilinolein.**

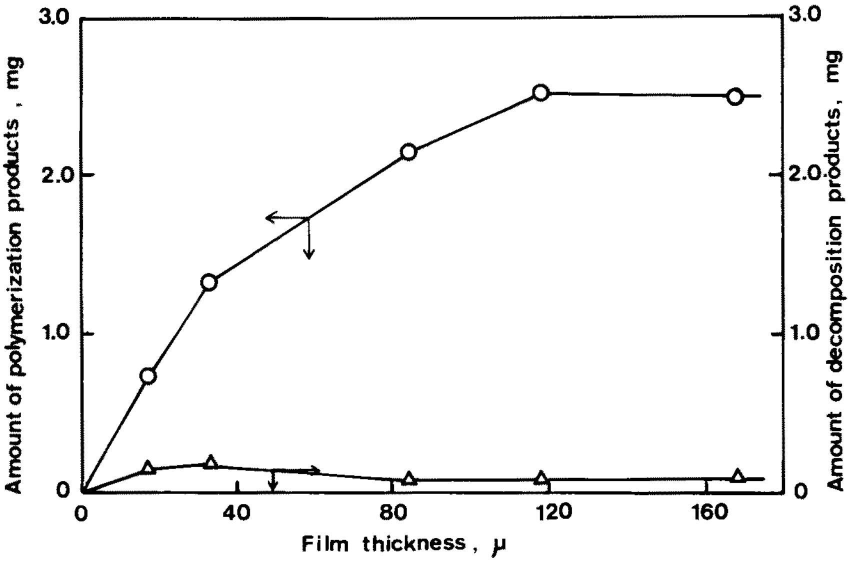

**FIG. 5. Relation between film thickness and thermal oxidation polymerization products and thermal decomposition products.**

seen in the figure, the residual weight fraction (ratio of residual weight to initial weight of sample) remains constant below 200 C, decreases rapidly in the range of 200-250 C and decreases gradually above 250 C. The dotted line in Figure 4a shows the vacuum thermogravimetric curve of unheated trilinolein. The result suggests that thermal decomposition and polymerization under a reduced pressure of $1 \times 10^{-5}$ mmHg don't occur within the temperature range 100 to 500 C. Therefore, the rapid decrease of residual weight fraction around 230 C and its gradual decrease above 300 C is considered to be due to evaporation of trilinolein and thermal oxidation polymerization products, respectively. Also, the residual weight fraction below 200 C increases with the increasing film thickness of the oil. The decrease is considered to be evaporation of volatile decomposition products including aldehydes, ketons, alcohols, esters, etc., during the heating process (11). It also can be seen from Figure 4 that a variety of compounds are formed during thermal treatment. The amounts of thermal oxidation polymerization and volatile decomposition products can be determined from these curves. The results are shown in Figure 5. In addition, the results obtained are schematically shown in Figure 6. It is evident from Figure 6 that the amount of thermal oxidation polymerization products increases with increasing thickness of film and peaches a constant value above 118 μ of film thickness, while the amount of decomposition products remains constant over film thickness of 0-170 μ. These results indicate that the oxidation reaction occurs only at the oil surface because of the diffusion of oxygen. Therefore, we may conclude that the oxidation reaction at the surface of the oil differs from that of bulk.

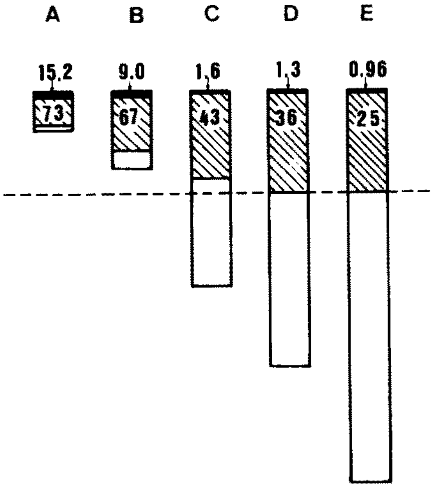

**FIG. 6. Relation between film thickness and thermal oxidation polymerization products and thermal oxidation decomposition products. Film thickness: A, 17 μ; B, 33 μ; C, 84 μ; D, 118 μ; E, 168 μ. Cross-hatched and filled areas indicated percentage of thermal oxidation polymerization products and thermal decomposition products, respectively.**

In order to study the time dependence of oxidation polymerization products, the vacuum TGA was carried out for trilinolein films of 80 μ thickness which were heated at 60 C of reaction temperature and for varying reaction times. The results at 60 min of reaction time are shown in Figure 7. The weight percent of polymerization products calculated from vacuum thermogravimetric curves of Figure 7 was plotted against reaction time at varying temperature. The results are shown in Figure 8. It is seen in Figure 8 that the percentage of oxidation polymerization products increases both with increasing reaction time and increasing reaction temperature. Therefore, the formation of oxidation polymerization is markedly influenced by reaction temperature and time.

Figure 9 shows the Arrhenius plots of thermal oxidation polymerization of trilinolein in air, which give two straight lines, one in the range of 40-80 C and the other in the range of 80-240 C. This suggests that the mechanism of thermal oxidation polymerization above 80 C may differ from that below 80 C. In the former, the apparent activation energy is about 19 Kcal/mol; in the latter, it is 5 Kcal/mol.

Further, the interaction between various metals and a thin film of oil is especially important in cooking. Thus, the thermal deterioration of trilinolein films on an iron pan in a nitrogen atmosphere was investigated and then compared with that on a platinum pan under the same conditions. Trilinolein was spread on iron and platinum pans to form a film thickness of about 80 $\mu$ and was then heated for 60 min at 200 and 250 C in a nitrogen atmosphere, and the vacuum thermogravimetric curve was obtained for trilinolein film of 80 $\mu$ thickness. Figure 10 shows the thermogravimetric curves of heated trilinolein on iron and platinum pans in a nitrogen atmosphere. As the amount of thermal polymerization products corresponds to the decrease in residual weight fraction above 300 C, it can be calculated from the decrease in residual weight fraction. The amount of thermal polymerization products at 200 C was determined to be 13.3% in the iron pan and 10.8% in the platinum pan, while at 250 C it was determined to be 37.8% in the iron pan and 15.9% in the platinum pan. Also, similar results are obtained for the amount of decomposition product. From these results, it was found that the iron pan accelerated thermal decomposition and polymerization of trilinolein faster than the platinum pan.

In addition, the effects of iron and silica pans on the thermal polymerization products were investigated. Figure 11 shows the rate of polymerization product against reaction temperature. It was found that in using the iron pan, the rate of polymerization products gradually increased from 200-230 C, and rapidly increased from 230-250 C with increasing reaction temperature, indicating that the polymerization became vigorous above 230 C. In the case of the silica pan, the rate of thermal polymerization products remained

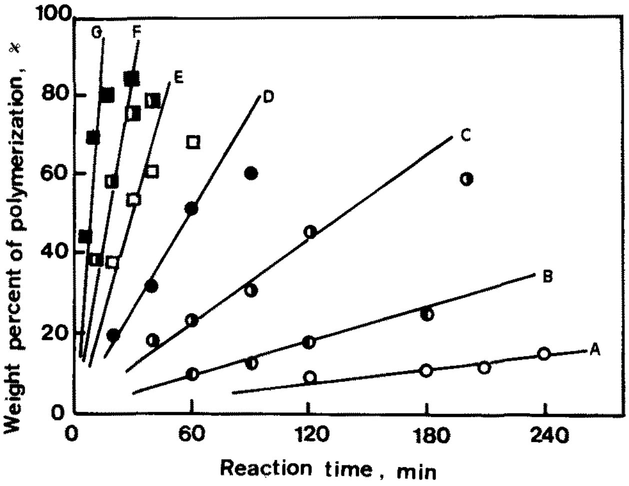

FIG. 8. Relation between reaction time and thermal oxidation polymerization products of trilinolein film (about 80 $\mu$) in air. A, 40 C; B, 50 C; C, 60 C; D, 70 C; E, 80 C; F, 100 C; G, 120 C.

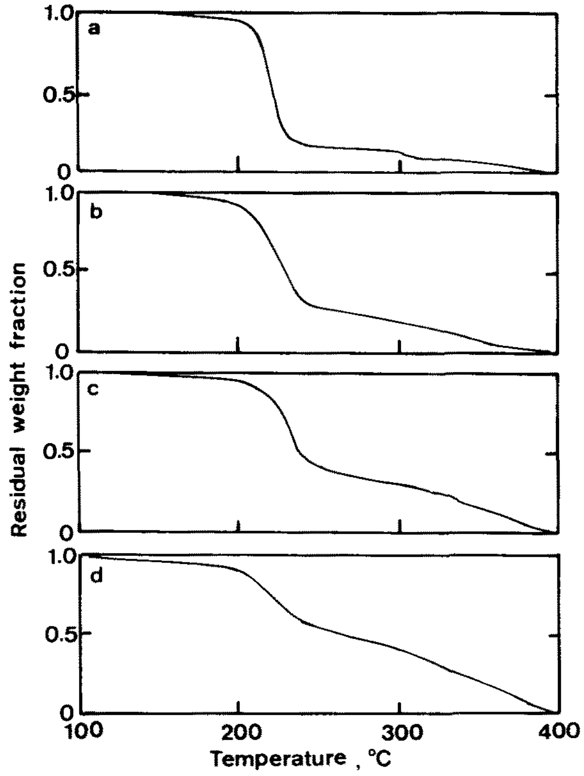

FIG. 7. Vacuum thermogravimetric curve of heated trilinolein in air. Reaction temperature, 60 C. Reaction time: a, 60 min; b, 90 min; c, 120 min; d, 200 min.

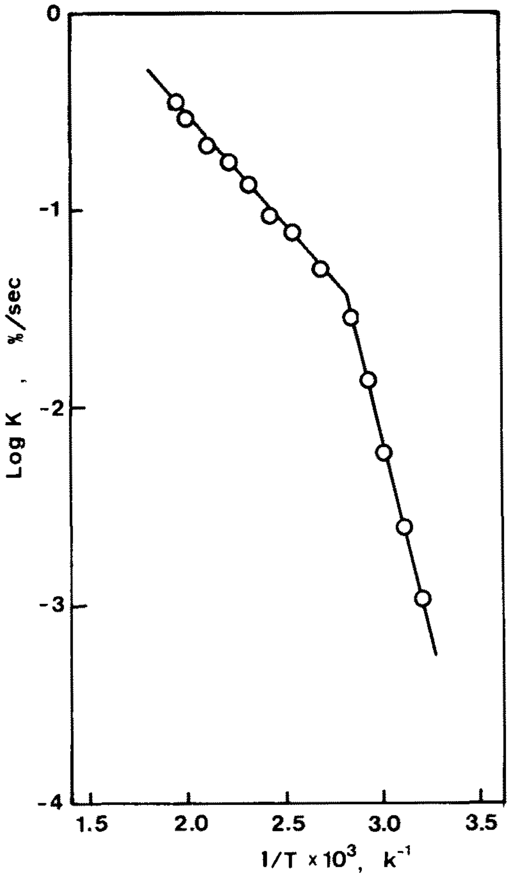

FIG. 9. Arrhenius plots of thermal oxidation polymerization of trilinolein in air.

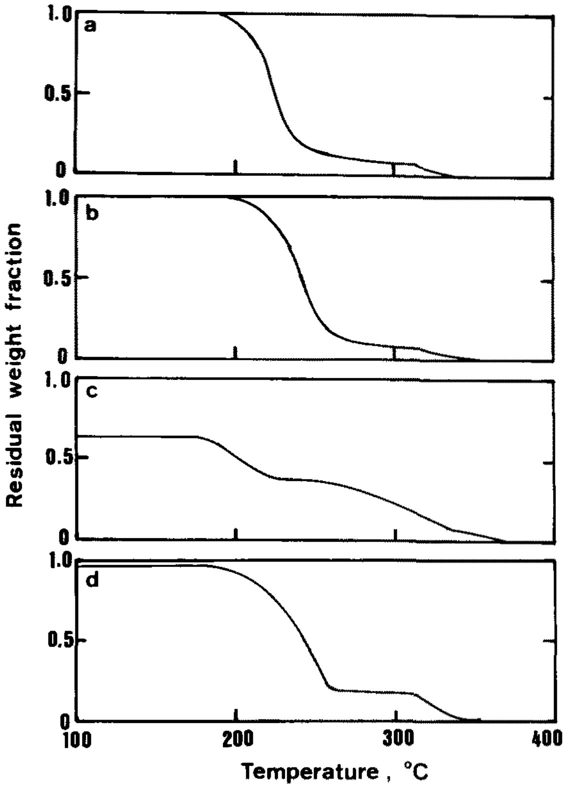

FIG. 10. Vacuum thermogravimetric curves of heated trilinolein on iron and platinum pans in nitrogen atmosphere. a, reaction temp. 200 C, Fe pan; b, reaction temp. 200 C, Pt pan; c, reaction temp. 250 C, Fe pan; d, reaction temp. 250 C, Pt pan.

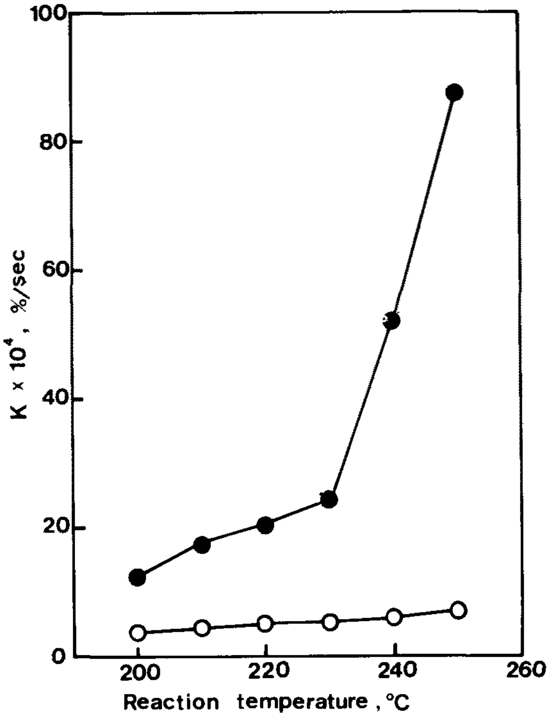

FIG. 11. Relation between reaction temperature and rate of thermal polymerization of trilinolein film on iron and silica pans in nitrogen atmosphere. ●——●, iron pan; ○——○, silica pan.

constant in the range of 200-250 C. Consequently, it was concluded that the thermal polymerization reaction is greatly affected by the iron pan above 230 C.

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