

Note

The DTA investigations of thermal resistance of autoxidation products cummulated in oxidized oleyl alcohol, oleic acid and methyl oleate

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The purpose of our work is to show and explain the influence of functional groups on the thermal resistance of the oxidation products of oleyl alcohol, oleic acid and methyl oleate. The following analytical methods were applied:

- (1) determination of peroxide number¹;
- (2) differential thermal analysis (DTA);
- (3) IR absorption spectroscopy.

The chemically pure sample of oleyl alcohol ("Fluka", Switzerland) had the following characteristics: iodine number, 88.0; peroxide number, 3.2; acid number, 1.7; refractive index, n_D^{20} , 1.462. The chemically pure sample of oleic acid (B. D. H. Chemicals Ltd., England) was characterized by the following numbers: iodine

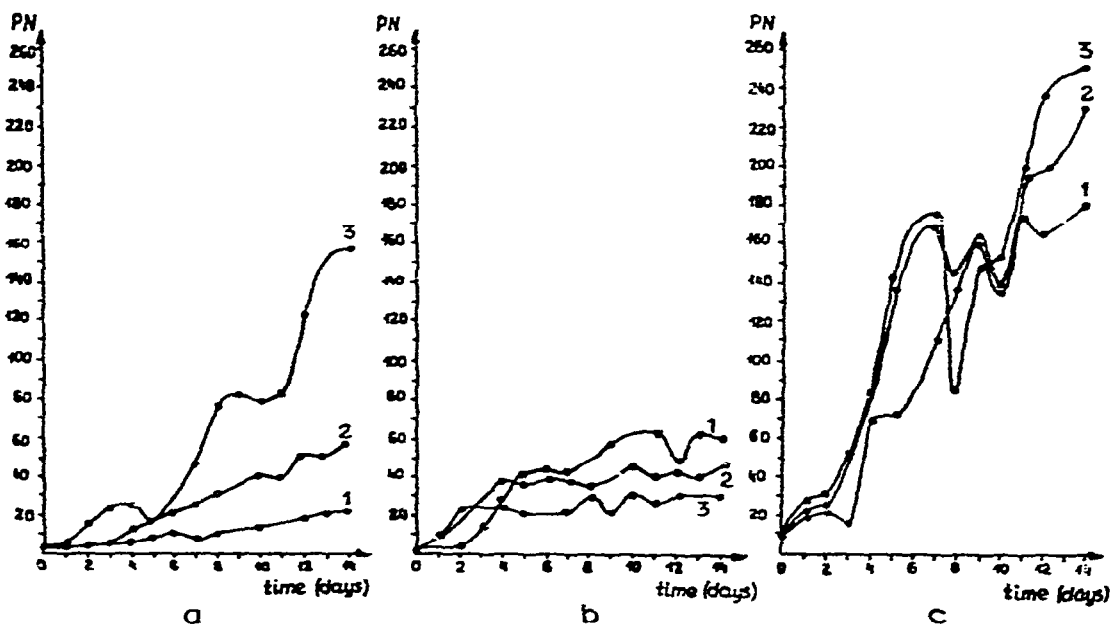


Fig. 1. Plots of peroxide number (PN) vs. time of oxidation at 1,40°; 2,50°; and 3,60°C for: a, oleyl alcohol; b, oleic acid; c, methyl oleate.

number, 94.3; peroxide number, 0.4; acid number, 198.1; refractive index, n_D^{20} , 1.463. The chemically pure sample of methyl oleate (prepared in our laboratory) had the following characteristics: iodine number, 90.1; peroxide number, 9.1; acid number, 21.1; refractive index, n_D^{20} , 1.456.

The 30-g samples of these compounds were incubated for 14 days at 40°, 50° and 60°C. At 24-h intervals the peroxide number of the samples was determined.

As seen in Fig. 1, the peroxide number levels of ester reached at three temperatures were relatively high and similar to one another. In the case of oleyl alcohol the following regularity was observed: the lower absorption rate of oxygen at lower temperature and the higher rate at higher temperature. Nevertheless, the peroxide number values of alcohol at all the temperatures were lower than those of ester. In the case of oleic acid the lower peroxide number values were related to the higher temperatures of autoxidation and vice-versa.

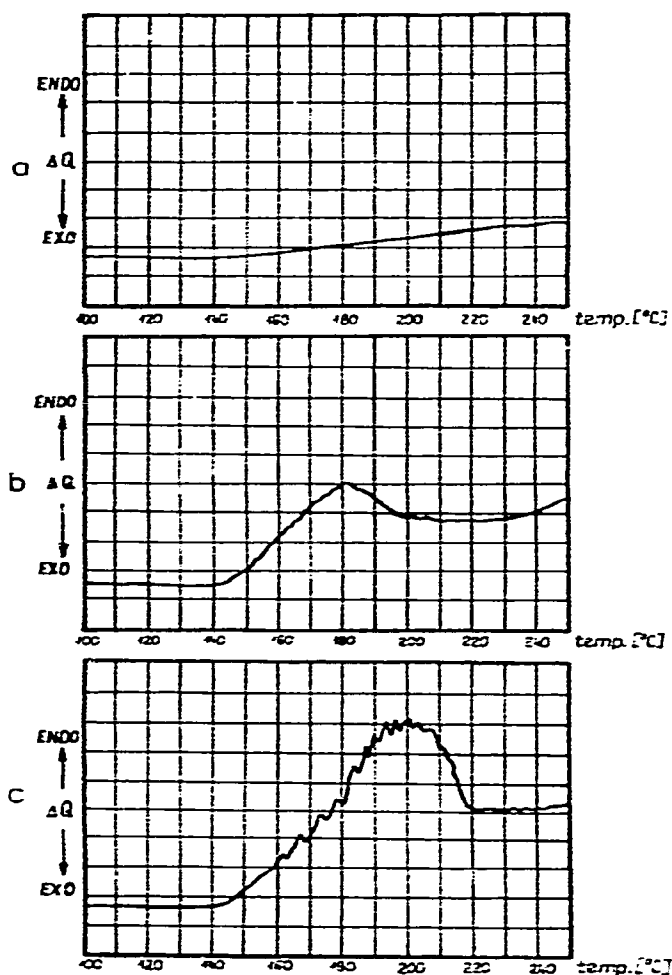


Fig. 2. The comparison of the DTA results in the case of: a, unoxidized oleyl alcohol; b, oleyl alcohol after 14 days of oxidation at 40°C; c, oleyl alcohol after 14 days of oxidation at 60°C.

The measurements, using differential thermal analysis (DTA) were performed before the beginning of autoxidation and at the end of this process at 40° and 60°C, the following conditions being used: mass of a sample, 10 mg; rate of heating, 8°C/min; argonium atmosphere; rate of registration, 20 mm/min. Analyses were performed using a Hitachi-Perkin-Elmer, Model DSC 1-B differential calorimeter. The purpose of DTA investigations was to determine the decomposition temperatures of hydroperoxide compounds, cummulated in the oxidized samples of oleyl alcohol, oleic acid and methyl oleate. In addition, we wished to obtain the graphical comparison of the amounis of these hydroperoxide compounds in each of our substrates. Figs. 2, 3, 4 and Table I show the results obtained.

Our investigations established that the highest decomposition temperature of the products of oxidation (147°C) characterized oleic acid, the lower one (141°C), oleyl alcohol, and the lowest one (117°C), methyl oleate. These results seem to agree

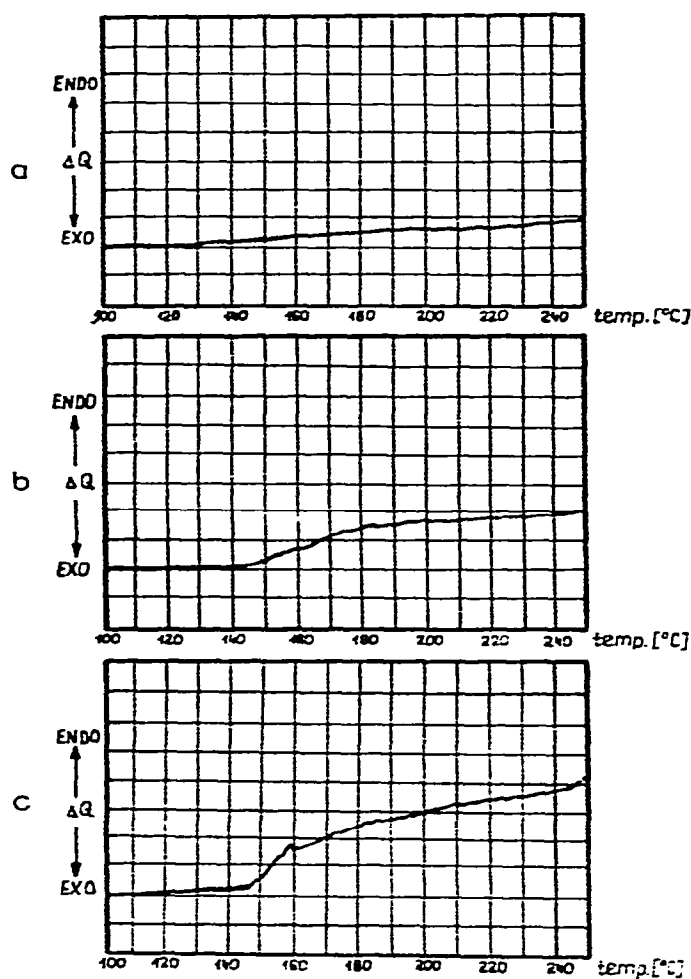


Fig. 3. The comparison of the DTA results in the case of: a, unoxidized oleic acid; b, oleic acid after 14 days of oxidation at 40°C; c, oleic acid after 14 days of oxidation at 60°C.

with the published data^{2,3}, recommending the range of temperatures lower than 120°C for analytical purposes in the chemistry of fatty compounds.

In order to explain the difference in the value of the peroxide number and the difference in the thermal resistance of autoxidation products, the possibility of

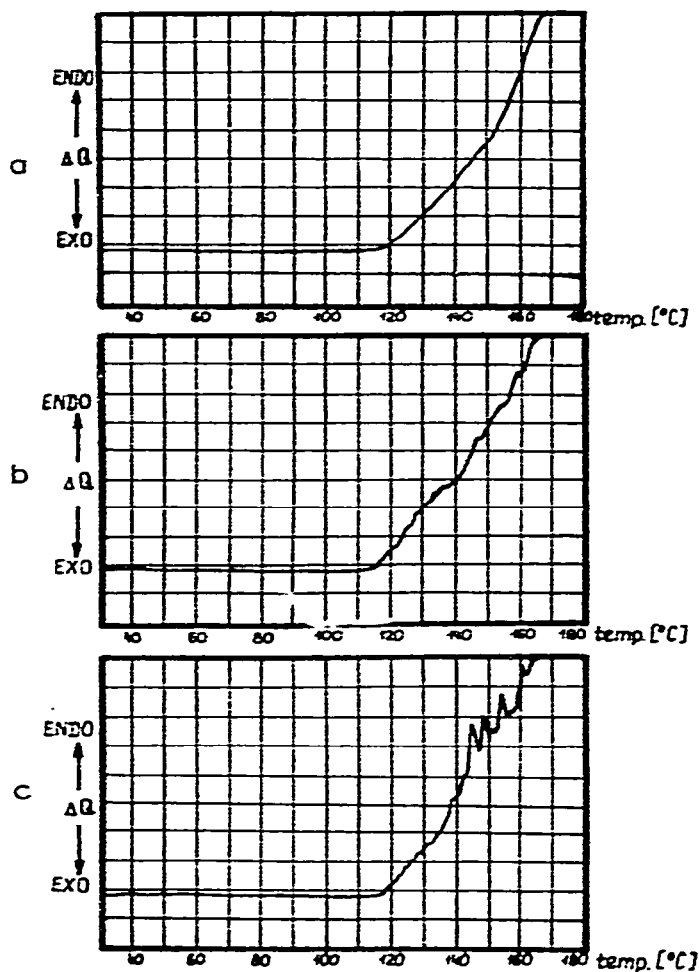


Fig. 4. The comparison of the DTA results in the case of: a, unoxidized methyl oleate; b, methyl oleate after 14 days of oxidation at 40°C; c, methyl oleate after 14 days of oxidation at 60°C.

TABLE I

THE COMPARISON OF THE DECOMPOSITION TEMPERATURES OF THE PRODUCTS OF AUTOXIDATION OF OLEYL ALCOHOL, OLEIC ACID AND METHYL OLEATE

<i>Reagent</i>	<i>Decomposition temperature (°C)</i>
Oleyl alcohol	141
Oleic acid	147
Methyl oleate	117

association by means of hydrogen bonds was examined for oleyl alcohol and oleic acid. Methyl oleate does not undergo comparable association because of the absence of the active (acidic) hydrogen atom. For this investigation, IR spectroscopic analyses were performed using a Spectromom 2000 (Hungarian) spectrophotometer.

The hydrogen-bonded, and non-bonded hydroxyl peak positions of alcohol and acid were determined in the following way: spectra were run for films of the examined compounds without any solvent (to determine the hydrogen-bonded hydroxyl peak positions), and for 0.0075 *M* solutions in CCl_4 (to determine the non-bonded hydroxyl peak positions). In the first case 0.025-mm absorption cells were used, in the second case, 2-mm absorption cells were used (Fig. 5).

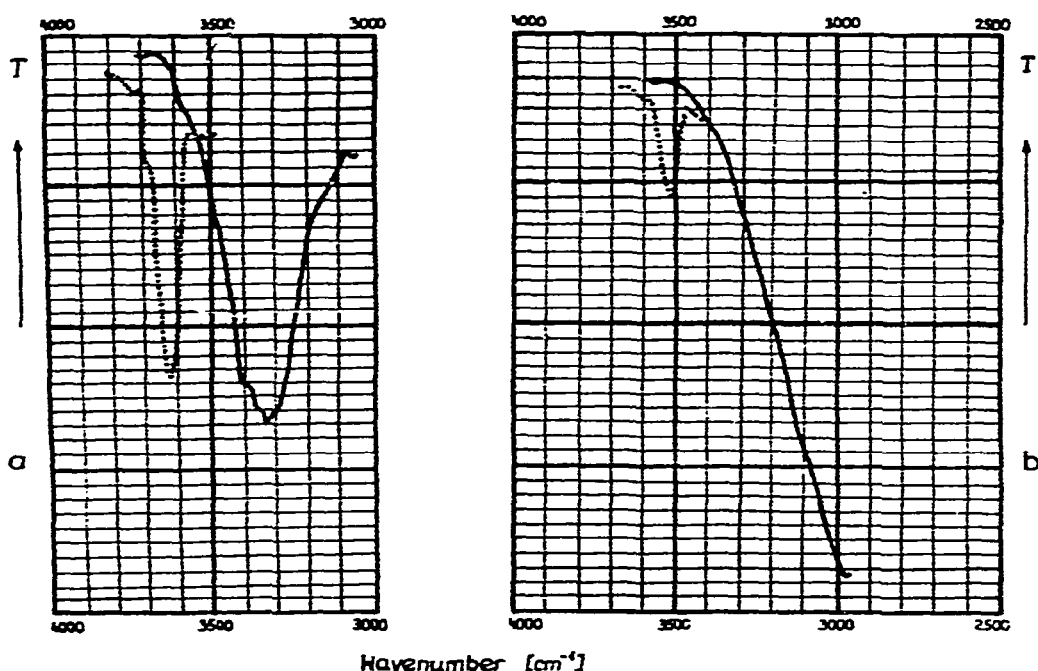


Fig. 5. The non-bonded (.....) and hydrogen-bonded (—) hydroxyl peak positions in the case of: a, oleyl alcohol; b, oleic acid.

The association shifts (in wavenumbers) of the hydroxyl peak positions are: 300 cm^{-1} in the case of alcohol and 540 cm^{-1} in the case of acid. These values may be considered a kind of measure of the strength of the hydrogen bonds, or more specifically of their enthalpy^{4,5}, and on this basis one may conclude about the greater strength of the hydrogen bonds in acid than in alcohol.

The influence of temperature on the intensity of hydrogen-bonded peaks was also examined (Fig. 6). In this case spectra were run at 18°, 40°, 50° and 60°C, using 0.025-mm absorption cells.

It can be seen that the change of temperature in the range 40°–60°C did not influence the diminution in intensity of the discussed peak in the case of acid, but influenced this diminution in the case of alcohol.

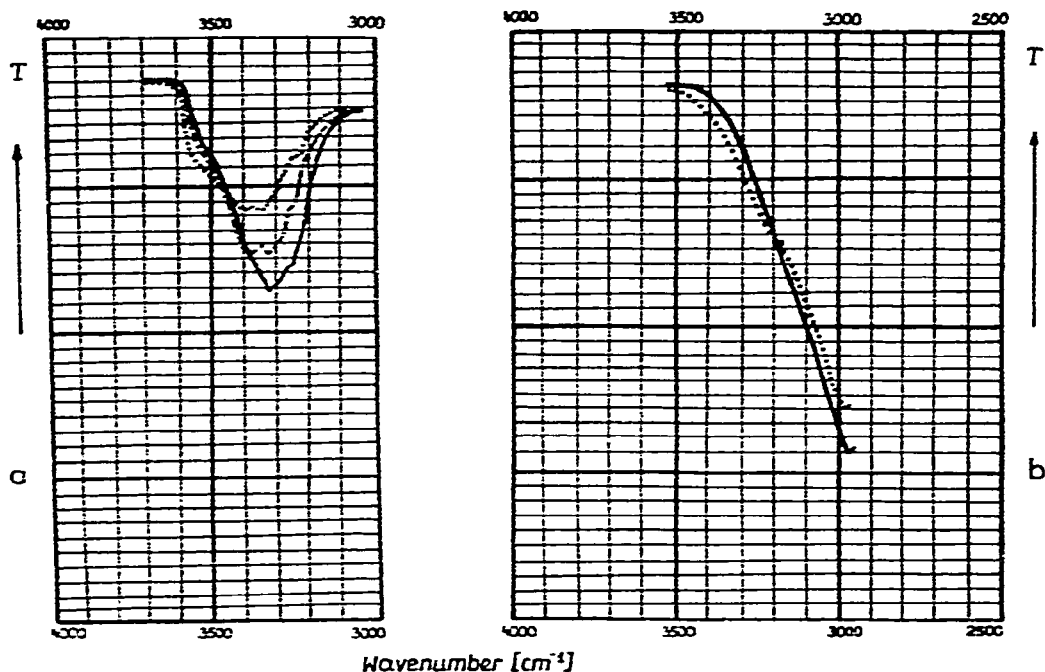


Fig. 6. The influence of temperature on the intensity of hydrogen-bonded hydroxyl peaks of: a, oleyl alcohol (—, 18°C; —.—.—, 40° and 50°C;, 60°C); b, oleic acid (—, 18°C;, 40°, 50° and 60°C).

Discussion

As shown in our report, the value of the peroxide number of the ester was the highest, and that of the acid the lowest. Correlation with the association leads one to conclude that the hydrogen association induces the greatest "stiffness" in the case of oleic acid and this "stiffness" is an obstacle in the development of the radical autoxidation process. On the other hand, methyl oleate may be said to yield the best conditions for the development of the free radical process. The DTA results sum up our considerations: because of their different degrees of association, the peroxides of oleic acid are the more resistant, and those of methyl oleate the less resistant, compounds.

REFERENCES

- 1 Polish Standards, PN-60/A-86918.
- 2 F. D. GUNSTONE AND T. P. HILDITCH, *J. Chem. Soc.*, (1945) 836.
- 3 K. S. MARKLEY, *Fatty Acids*, Interscience, New York, 1947, p. 452.
- 4 R. F. BADGER, *J. Chem. Phys.*, 8 (1940) 288.
- 5 M. L. HUGGINS AND G. C. PIMENTEL, *J. Phys. Chem.*, 60 (1956) 1615.