SHORT COMMUNICATIONS

POLAROGRAPHIC STUDIES ON DIF-FERENT TYPES OF PEROXIDES AND ALLIED MATERIALS FROM AUTOXIDIZED FATS

The peroxides may be taken as auto-oxidation products which are capable of oxidising iodide ions to iodine. Several types of structure which react in this manner occur in oxidised fats. The auto-oxidation products of fats include more than one type of peroxide structure and in many cases several structures of a given type co-exist in an oxidation mixture.

The theories concerning the machanism by which atmospheric oxygen reacts with fats have been reviewed by different workers. Recent investigations have shown that hydroperoxides are the structures which predominate in autoxidized fats. Compounds of this type have been isolated by Farmer[6] and also by Swift et al.[7] and Khan.[19] The products isolated from autoxidized methyl oleate consisted of a mixture of the two possible isomeric hydroperoxides. In poly-unsaturated fatty acids, there may be several isomeric hydroperoxides for each fatty acid. Absorption spectral data indicate that the conjugated isomers which arise as a result of the position of electrons are present in the largest amounts. Moreover, the differences in characteristics due to geometric isomerisms [8-9] in these peroxides may be useful in distinguishing them.

The behaviour of individual peroxide structures is not known with certainty, largely because there has been no analytical procedure available which could determine individual peroxide structures in the presence of other fat peroxides. Lack of direct means for the qualitative and quantitative determination of the auto-oxidation products has been a handicap in such work. It seems, however, possible that the polarograph might be capable of selectively reducing fat peroxide in auto-oxidised fats and volatile products from them ~~in auto-oxidized fats and volatile products from them~~.

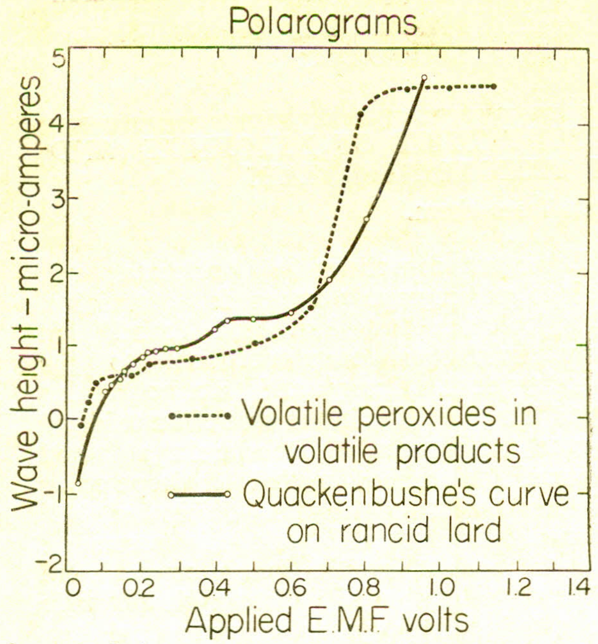
Lewis and co-workers [10-11] obtained well-defined polarographic waves for autoxidized methyl oleate, and lard and found that wave heights were proportional to the concentrations. Bovey and Kolthoff[12] also found this to be true in the case of autoxidized styrene polymers. Dobringskaya and Neiman[13] determined methyl hydroperoxide mixtures with aldehydes. Swern et al.[14] claimed fair results with various fat peroxides.

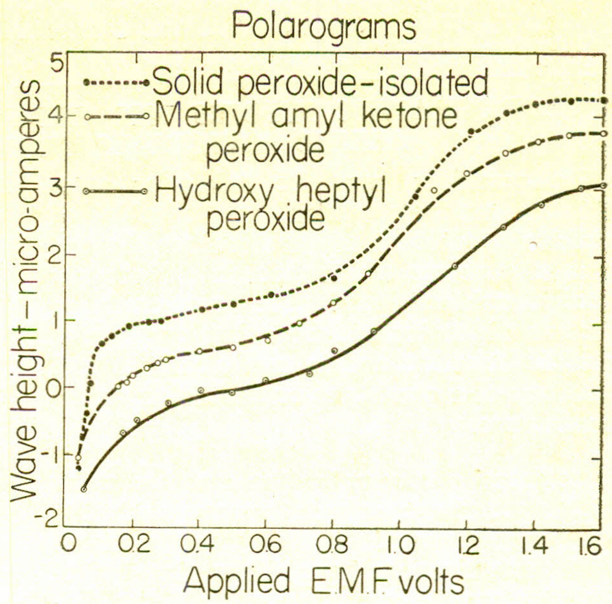
In the present investigation, attempts were made to determine and distinguish peroxide products in volatile products from autoxidized methyl oleate and stearolate. Some known peroxides of carbonyl type and also methyl oleate, linoleate hydroperoxides with their geometric isomers have been subjected to investigation. The procedures for polarographic studies were exactly the same as those used by Lewis et al.

Experimental.

The solid peroxides were obtained by crystallizing 30% solution of volatile products from autoxidized methyl oleate and stearolate[15] in heptane (unsaturate-free) at 60°C. Methyl amyl ketone peroxide, hydroxy heptyl peroxide and t-butyl peroxide were obtained as pure chemicals from the market. Methyl oleate and linoleate hydroperoxides were obtained by countercurrent extraction[16].

The polarographic studies indicated multiple peroxides with one kind predominating in the total volatile products from the autoxidized methyl oleate. The curves (Fig. 1) were also identical to those obtained from volatile products of autoxidized methyl stearolate and ordinary fats. Such similarities are probably





due to their common origin. Methyl oleate and methyl stearolate have the following structures:

$$CH_3\,(CH_2)_7\,CH = CH\,(CH_2)_8\,COOCH_3\cdot$$
$$CH_3\,(CH_2)_7\,CH \equiv CH\,(CH_2)_7\,COOCH_3$$

Both have a common segment CH (CH_2), which is also common in ordinary fats. This may mean that decomposition during autoxidation has involved this segment in yielding the volatile products. Furthermore, volatile peroxides show three types of peroxides similar to those in autoxidized lard (Fig. 1).

The solid sample of peroxide from these volatile products gave similar curves to known ketone and aldehyde peroxides (Fig. 2). The solid peroxide was found to be polymeric in nature. It is evident that the solid is a carbonyl type of peroxide, not specifically identified. From these findings, it may be said that polarographic studies may establish the types of peroxides, if the corresponding known standards are available. Oleate and linoleate hydroperoxides could not be well distinguished. Their half-wave potentials were very close together. Similarly, methyl elaidate hydroperoxide,[17] *Cis, trans*-linoleate and *trans, trans*-linoleate conjugated hydroperoxides[18] and methyl linoleate 11-hydroperoxide[17] behaved the same way. As a matter of fact, the hydroperoxide could be differentiated from other peroxides. Hence, when we had a known standard, the purity of another known peroxide of similar structure could be established. The most important point is that one polarographic half-wave potential may represent similar peroxides of many types, and a decision about the peroxidic structure may be reserved, until further confirmatory evidence is available. Once the instrument is standardized for one definite peroxide, the peroxides of the same nature may be established by polarographic analysis.

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