Kinetic Investigations into the Metal Catalysed Autoxidation of Methyl Linoleate

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It has long been known that the oxygen absorption by linseed and other drying oils on exposure to air and the drying process caused by this absorption is accelerated by certain metal salts (so-called siccatives). Among the most important of these salts for practical use are ones involving cobalt, lead and manganese. However, the kinetics of these reactions have been studied only during the last three decades, and then with partly contradictory results. Eibner and Pallauf¹ found that the drying time for linseed oil, reduced with a constant, was inversely proportional to the siccative concentration. Bowles² found in a research upon cobalt-siccativated stand oils that the drying time was inversely proportional to the square root of the cobalt concentration, and Lund³ arrived at similar results in researches upon cobalt and manganese siccatives in linseed oil.

Apart from some experiments on the weight increase on exposure to air of thin oil films on glass (so-called Weger curves) and some introductory oxygen absorption measurements by Lund³, the earlier investigations were limited to researches upon the relationship between the metal concentration and drying time as determined in a more or less subjective manner. Hereby the drying process was allowed to proceed to a far advanced stage, when the primary phase, the autoxidation, had been followed to a great extent by the secondary one, involving the formation of a tackfree gel of makromolecules.

Our researches have especially aimed to try to establish the reaction mechanism of the metal catalysed autoxidation. It was thereby considered to be necessary to work with a compound of a less complicated composition than linseed oil. As such a compound methyl linoleate was chosen.

The autoxidation has been followed by measuring the oxygen absorption at constant pressure and temperature (25° C) in an apparatus constructed for

Fig. 1. The oxygen absorption of methyl linoleate as a function of the reaction time in the presence of

- I. $[Co] = 2.88 \cdot 10^{-6}$ mol per g
 II. $[Mn] = 3.09 \cdot 10^{-6}$ » » »
 III. $[Pb] = 10.85 \cdot 10^{-6}$ » » »

this purpose and which is essentially similar to the Warburg apparatus. The metal catalysts studied were cobalt, lead and manganese salts of α -ethyl caproic acid. These salts are used as siccatives in the paint industry under the name octoates.

Methyl linoleate from two quite different sources was used and gave identical results. Through special experiments it was demonstrated that the vibration velocity of the reaction vessel (240 strokes/min) was sufficient to insure that the diffusion of oxygen into the reaction mixture would not influence the results.

Our experiments have proved that the reaction velocity, determined by the oxygen absorption per minute, after a variable induction period reaches a value that is constant within the experimental errors (Fig. 1). This constant reaction velocity depends on the metal concentration (Fig. 2) and on the methyl linoleate concentration (Fig. 3) but only slightly on the oxygen pressure within the studied range ($\frac{1}{2}$ —1 atm). Through determinations of the peroxide content in the reaction mixture at the end of some experimental series, it has been demonstrated that the absorbed oxygen, calculated from the absorption measurements, is found almost quantitatively as peroxide.

It immediately appears from Fig. 2 that the reaction velocity cannot be proportional to the metal concentration. A mathematical analysis of the present values also shows that proportionality between the velocity and the

Fig. 2. The dependence of the reaction velocity on the metal concentration in undiluted methyl linoleate.

- I. Cobalt
- II. Manganese
- III. Lead

Fig. 3. The dependence of the reaction velocity on the methyl linoleate concentration.

- I. $[Co] = 3.3 \cdot 10^{-6}$
- II. $[Mn] = 4.0 \cdot 10^{-6}$
- III. $[Pb] = 5.8 \cdot 10^{-6}$

$[RH]$ = the methyl linoleate concentration in parts by weight.

square root of the metal concentration does not entirely agree with the experimental data. The analysis indicates a parabolic function

$$v^2 + \alpha \cdot v = \beta \cdot [Me]$$

where v = the oxygen absorption velocity (mol O_2 /mol linoleate and min)
 $[Me]$ = the metal concentration (mol/g reaction mixture)
 α and β are two factors primarily dependent upon the methyl linoleate concentration, but to a less extent probably also upon the oxygen and peroxide concentrations, but independent of $[Me]$.

It should be observed that lead, in contrast to what is often stated, also catalyses the primary oxygen absorption.

Through researches by Farmer, Bolland, Bergström, and many others it can be regarded as proved that the first comprehensible reaction product in the autoxidation of organic compounds with one or more isolated double bonds is a hydroperoxide with the atom group $-OOH$ at a single carbon atom

and with the double bonds still intact. Bolland and Gee⁴ have also made it probable that the reaction follows a chain mechanism with free radicals as chain carriers.

It is fairly reasonable to assume that the metal catalysed autoxidation follows a similar chain mechanism. However, the chain carriers are here probably addition products between the metal and the methyl linoleate and probably with radical character. The following reaction scheme has proved to be able to explain the above-mentioned formula

1. $\text{Me} + \text{ROOH} \rightarrow \text{MeO}_2 + ?$
2. $\text{MeO}_2 + \text{RH} \rightarrow \text{RMeO}_2$
3. $\text{RMeO}_2 + \text{RH} \rightarrow \text{ROOH} + \text{RMe}$
4. $\text{RMe} + \text{O}_2 \rightarrow \text{RMeO}_2$
5. $2 \text{RMeO}_2 \rightarrow 2\text{Me} + \text{inactive end product}$
6. $\text{RMe} + \text{RMeO}_2 \rightarrow 2 \text{Me} + \text{inactive end product}$
7. $2 \text{RMe} \rightarrow 2 \text{Me} + \text{inactive end product}$

where

RH symbolizes methyl linoleate

R symbolizes methyl linoleate that has lost one methylenic hydrogen atom

ROOH symbolizes methyl linoleate hydroperoxide

To get theory and experiments to coincide, the metal should be present at the initiation reactions 1. and 2. in an activated state, the concentration of which is but a small portion of the total metal concentration. The reactions 3. and 4. represent the propagation reactions with RMeO_2 and RMe as chain carriers. Among the chain termination reactions (5., 6. and 7.) 5. is under the present conditions, high oxygen concentration, so predominant that 6. and 7. can be neglected. The initiation reaction 1. explains the observed induction period.

The researches will be continued in different directions. A full report of the process catalysed by cobalt, lead or manganese will appear within a short time.

SUMMARY

The autoxidation of methyl linoleate in the presence of cobalt, manganese and lead compounds has been examined by measuring the oxygen absorption velocity. It has been shown that these metals catalyse the autoxidation, but the influence of lead is less than that of the others. The autoxidation velocity depends on the metal concentration, the methyl linoleate concentration and — to a less extent — the oxygen pressure. From the experimental data it seems probable that the reaction follows a chain mechanism similar to the one

which prevails at the uncatalysed autoxidation. However, the chain carriers are probably addition products, with radical character, between the metal and the methyl linoleate.

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