

## Effect of Some Transition Metals on the Monolayer Oxidation of Methyl Linoleate

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**Abstract** Methyl linoleate was deposited as a monolayer on a silica gel control and on silica gel supplemented with double or quadruple the control's amount of the transition metal ions (TMI) iron, copper, vanadium or titanium. The treatments were oxidized at 25 °C, and periodically samples were examined for peroxide values (PV) and by gas chromatography for oxidation products (GC). Comparison of the treatments revealed that: Surface oxidation on silica gel owes its high rate to TMI, which may speed free radical initiation. Epoxidation is catalyzed by the presence of vanadium and titanium. Scission products (SP) and unrecovered mass increased with the extent of oxidation probably because of increased free radical life time.

**Keywords** Surface oxidation · Transition metal ions · Methyl linoleate · Oxidation products · Kinetics

### Introduction

Unsaturated fatty acids (PUFA) spread on surfaces oxidize most rapidly when present in amounts that form a monomolecular layer, and these rates are 8–10 times greater than

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that of bulk PUFA [1–3]. The oxidation of PUFA in monolayers follows pseudo first-order kinetics and produces significant amounts of epoxidized products in contrast to oxidation in bulk PUFA [3–5]. Tekin and Hammond [5] reported that the chief non-scission products (NSP) of methyl linoleate oxidation were epoxy (E), hydroxy (H), hydroxy-epoxy (HE) and dihydroxy (DH) fatty acid methyl esters (FAME). They found the greatest non-scission product (NSP) concentrations were attained when the PV reached a maximum. Porter et al. [3] showed that acid treatment of the silica, which reduced its iron content, and chelation agents slowed oxidation. TMI affect the rate of oxidation and probably the rate of free radical formation [6]. Titanium and vanadium catalyze epoxidation reactions [7], but the roles of these elements in monolayer oxidation have not been studied.

The objective of this study was to determine the effects of TMI on the surface oxidation of methyl linoleate on silica gel and to obtain deeper insights into the mechanisms of surface oxidations.

### Experimental Procedures

#### Materials

Methyl linoleate (99+% pure), methyl palmitate (99% pure), silica gel H, vanadium (III) acetylacetonate (97%) and titanium (IV) propoxide (98%) were purchased from Sigma-Aldrich. Ferrous sulfate, cupric sulfate and other analytical-grade solvents and chemicals were from Merck.

#### Methods

To determine the mineral content of silica gel H, a 0.1-g sample and 4 mL HCl/HNO<sub>3</sub> (3:1 v/v) were heated in a

microwave oven in a sealed vessel at  $\sim 100$  °C for 30 min. The acid layer was analyzed by Plasma-Optical Emission Spectroscopy for iron, copper, vanadium and titanium. Aqueous solutions of these ions were added to silica gel to increase the amounts of these metals two and four fold. This required the addition of 200 and 400 ppm iron, 2 and 4 ppm copper, 20 and 40 ppm vanadium and 200 and 400 ppm titanium to silica gel. The metals were dissolved in water and mixed with silica gel for 1 h and dried at 105 °C.

For the preparation of methyl linoleate monolayers on silica,  $2.00 \pm 0.01$  g of methyl linoleate and 105.26 mg of the methyl palmitate internal standard were dissolved in 30 mL hexane and added to  $8.00 \pm 0.01$  g of Silica gel H [8]. After stirring for 2 min, the hexane was evaporated under reduced pressure, and the residues were oxidized at 25 °C.

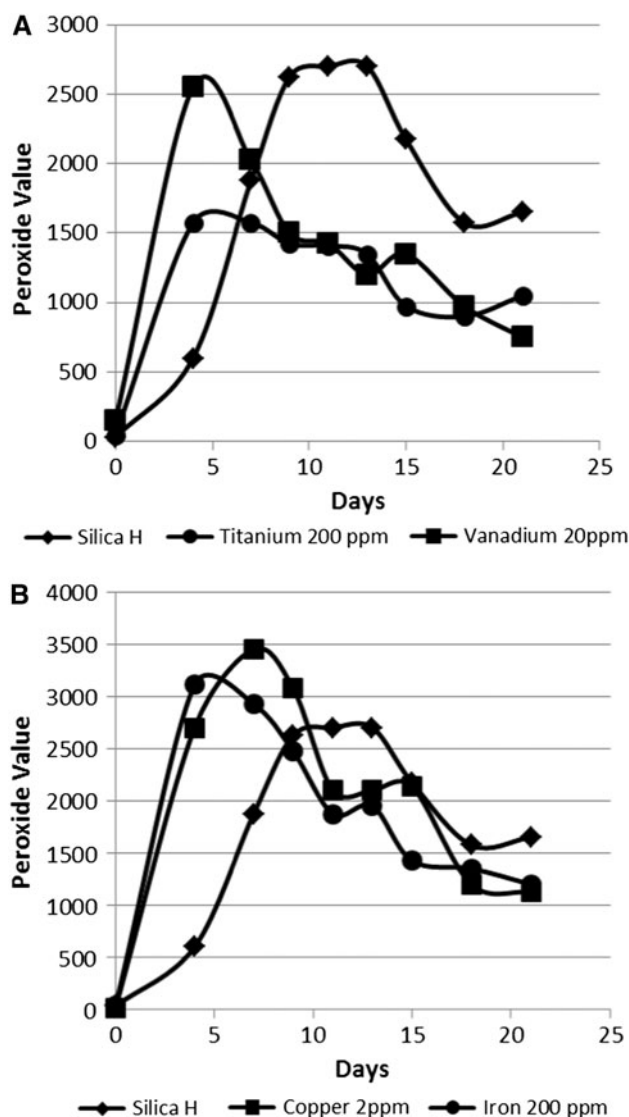
#### Analysis of Oxidation Products

Periodically 0.8 g samples were withdrawn, the PV was measured [9] without removing the silica. Next the silica was removed by filtration, and the filtrate was washed three times with  $\sim 30$  mL of water to remove acetic acid, and the chloroform was evaporated. The residue was dissolved in hexane and analyzed by GC for oxidation products as described previously [5].

#### Results and Discussion

Complete data from these experiments are available as Electronic Supplementary Material. Figure 1 compares the PV of the silica control oxidized at 25 °C with silica containing added TMI. All the TMI increased the oxidation rate and caused the PV to reach a maximum earlier than the control. Copper and iron additions resulted in greater PV maxima than the control, but the PV maximum for vanadium was similar to the control, and that of titanium was smaller. The PV decline after the linoleate concentration dropped to less than  $\sim 10\%$  of its original value. This drop in PV probably occurred because the hydroperoxides were being converted to other products, and the declining linoleate concentration could not sustain a high PV.

The more rapid attainment of PV maxima when transition metal ions were added suggests that all the TMI increase the rate of the chain reaction by increasing free radicals initiation. The rapid oxidation of lipids monolayers seems to depend on the presence and proximity of TMI [3, 5]. However, facilitated transfer of oxygen in the monolayer, the moisture content [10] and possibly the alignment of the lipid molecules on the surface also may affect rates.



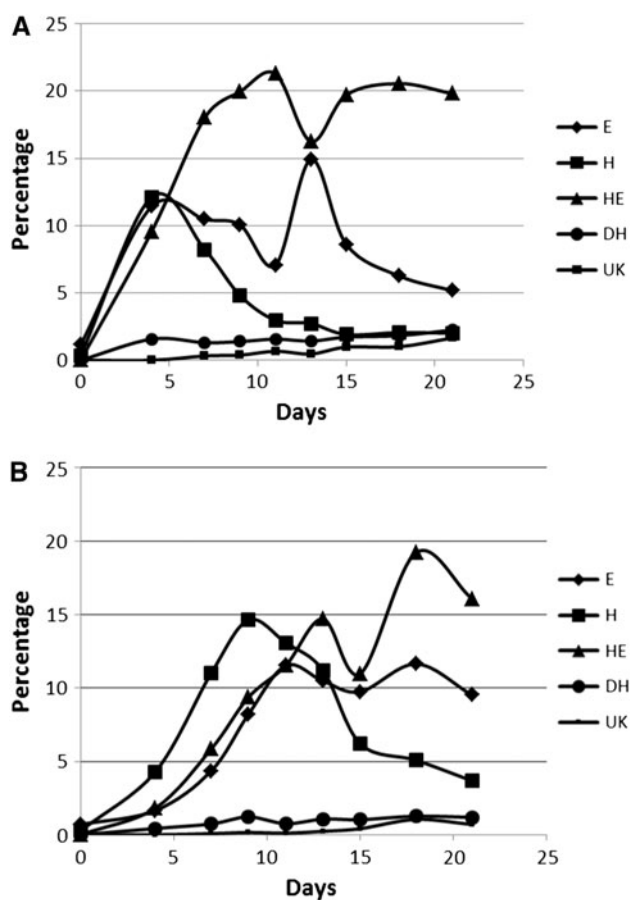
**Fig. 1** Peroxide values versus time for the surface oxidations of methyl linoleate at 25 °C. **a** Compares the control with treatments containing an additional 200 ppm iron or 2 ppm copper. **b** Compares the control and treatments with an additional 200 ppm titanium or 20 ppm vanadium

Linoleate disappearance with time for all treatments followed pseudo first-order kinetic as noted previously [3–5]. Linear plots of the logarithm of the linoleate concentration versus time accounted for  $>98\%$  of the variance.

In bulk autoxidation of methyl linoleate, the rate of initiation of free radicals is a function of the square of the hydroperoxide concentration, and the reaction is autocatalytic [11]. The first order kinetics of surface oxidation is not completely explained by the reaction of TMI with hydroperoxides [6]. There may be a period at the beginning of oxidation when the rate of linoleate disappearance is increasing slightly as the PV increases [5] as would be expected. But the rate eventually becomes approximately

constant in spite of further variation in the PV. Possibly, at a constant oxidation rate the rate of initiation depends on the rate of diffusion of a hydroperoxide to a TMI surface in this unstirred system. A dependence on diffusion would also account for the maximum rate being observed near the monolayer concentration.

Figure 2 shows typical changes with time in the concentration of E, H, HE, DH and an unknown (UK) for the control and for the sample with 200 ppm vanadium at 25 °C. The vanadium sample produced H and HE more quickly and contained more HE than the control. Vanadium, and to a lesser extent titanium, catalyzed the formation of epoxides [7]. Probably the reason that samples containing vanadium and titanium do not attain as high a PV maxima as controls (see Fig. 1) is because E and HE formation consumes hydroperoxides, which may reduce the rate of the chain reaction, especially in the early stages of oxidation. In accord with this theory Fig. 2 also shows that with time, the concentration of H peaked and then declined as E and HE increased. It is difficult to follow



**Fig. 2** The percentage of methyl linoleate recovered as epoxy (E), hydroxy (H), hydroxy-epoxy (HE), dihydroxy (DH) and unknown (UK) derivatives during surface oxidation at 25 °C. **a** Shows the control and **b** the treatment with 20 ppm added vanadium

these reactions accurately because the amounts of H and HE that are measured can include both hydroperoxides and their alcohol reduction products. At times the amounts of H and HE are too small to account for the observed PV. This discrepancy between the PV and observed H and HE increased to a maximum at the PV maximum, and then declined. Similar data were obtained by Tekin and Hammond [5], and may be caused by a poor response of hydrogen flame detectors to the reduced form of H [12].

Figure 2 shows that the production of E and HE does not follow a smooth curve. This variation may be caused by a lack of uniformity of TMI distribution on the silica.

Figure 2 also shows the formation of small concentrations of DH and an unknown product, UK. The amounts of both products are increased slightly by the addition of TMI. The DH slowly rises with time and may be produced by ring opening of E because of the acid conditions in the reductive isolation process. The UK may be a trihydroxy compound produced similarly from HE, but it is not completely identified. The UK tends to be present in smaller percentages than DH and often is undetectable in early samples.

Scission products, which represent oxidation products with retention times less than that of methyl linoleate, increase slowly with oxidation time from <1 to 39–56% of the GC area of the original methyl linoleate. The total GC peak area that is recovered also decreases with oxidation time from 94 to 68–77%. These calculations ignore the possible difference in GC response to the various oxidation products, and the true loss may be overvalued [12]. The formation of polymers and very volatile scission products, which are not detected under our GC conditions, also account for some of the loss. The loss tends to parallel the formation for SP, probably because both depend on free radical reactions. As the methyl linoleate levels decline with oxidation so does that of easily extracted hydrogen that can terminate reactions chains. The decline of this hydrogen source may prolong the time during which scission and polymerization can occur and account for the increase in SP and the loss of peak area with oxidation time.

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