# Some Effects of Pressure on the Oxidation of Methyl Oleate

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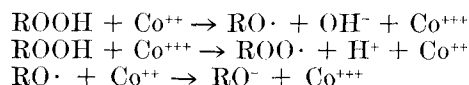
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The oxidation of methyl oleate under gas pressures up to 800 p.s.i.a. has been investigated. At 120°C. the samples oxidized under pressure built up hydroperoxides rapidly and exploded. There is no necessary connection between hydroperoxide concentration and explosiveness. Oxidations at 100°C. are stable, but peroxide formation is drastically reduced. The presence of cobalt acetate increases the instability of the oxidizing oleate, causing it to explode even at 100°C.

IN THE WORK carried out in this laboratory on the autoxidation reaction of unsaturated fatty acids and esters as a possible preparative method, various ways of modifying the reaction have been investigated. Means of accelerating the reaction, as well as of maximizing yields of hydroperoxides and secondary oxidation products, have been considered. Pressure is known to be a significant variable in this reaction. The literature on the effect of superatmospheric pressures however is not extensive. Matsumoto and Ichiro (7) oxidized various oils under 10–20 atmospheres and found that pressure increased the peroxide yield. Patrick and Emerson (8) oxidized oleic acid, ethyl and methyl oleate at air pressures up to 200 p.s.i. and found that increasing pressure increased the yield of short-chain scission products. Their starting materials however contained high percentages of polyunsaturates, which would strongly affect the course of the autoxidation reaction.
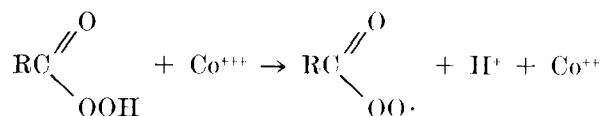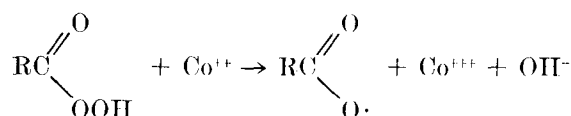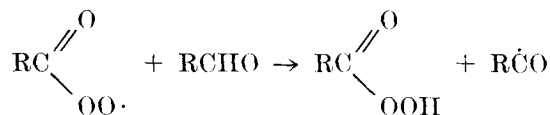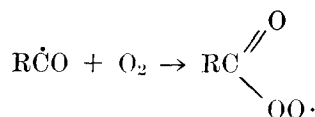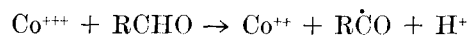
Gearhart *et al.* (2) observed that vegetable oils at about 100°C. exploded under 100 p.s.i. of $O_2$ but not under 50 p.s.i., indicating a strongly pressure-dependent oxidation reaction. Therefore the possibility of carrying out autoxidations under even higher pressures was considered. A preliminary experiment was carried out in which a 25-g. sample of purified methyl oleate was oxidized at 100°C. under 1,400 p.s.i. $O_2$. After about $3\frac{1}{2}$ hours the reaction exploded. This paper is limited to defining some of the safety limits in working with pressure and attempting to obtain maximum yields of hydroperoxides and acids within these limits. Oxidations have been carried out both with and without a catalyst.

In autoxidation, hydroperoxides are initially formed, which through chain scission and further oxidation are converted into shorter chain mono- and dibasic acids. Complete conversion of pure methyl oleate to its monohydroperoxide would result in a product with a peroxide value of 6,088 meq./kg. If this hydroperoxide were quantitatively split and the fragments oxidized to mono- and dibasic acids, without loss of $CO_2$ or other side products, the resulting mixture would have an acidity of 5,548 meq./kg. These figures represent optimum and doubtless unattainable yields but are useful in assessing the efficiency of an oxidation procedure.

Multivalent metal ions have a dual catalytic function in autoxidizing unsaturated systems. They catalyze the decomposition of hydroperoxides to give free radicals that can start new chains. For example (6):

$$ROOH + Co^{++} \rightarrow RO\cdot + OH^- + Co^{+++}$$
$$ROOH + Co^{+++} \rightarrow ROO\cdot + H^+ + Co^{++}$$
$$RO\cdot + Co^{++} \rightarrow RO^- + Co^{+++}$$

The principal oxygen attack occurs at a methylene group $a$ to a double bond to give an $a,\beta$-unsaturated hydroperoxide. These can decompose in a number of ways into fragments, such as carbonyls, which can be further oxidized to acids. Metal ions also play a role in this secondary oxidation, as shown in the series of reactions (1):

$$Co^{+++} + RCHO \rightarrow Co^{++} + R\dot{C}O + H^+$$

$$R\dot{C}O + O_2 \rightarrow RC \overset{O}{\underset{OO\cdot}{\big<}}$$

$$RC \overset{O}{\underset{OO\cdot}{\big<}} + RCHO \rightarrow RC \overset{O}{\underset{OOH}{\big<}} + R\dot{C}O$$

$$RC \overset{O}{\underset{OOH}{\big<}} + Co^{++} \rightarrow RC \overset{O}{\underset{O\cdot}{\big<}} + Co^{+++} + OH^-$$

$$RC \overset{O}{\underset{OOH}{\big<}} + Co^{+++} \rightarrow RC \overset{O}{\underset{OO\cdot}{\big<}} + H^+ + Co^{++}$$

## Procedure

Purified methyl oleate [iodine value (IV), 83.6] was used for all oxidations. A Parr medium-pressure reaction vessel was modified to allow a small sample to be oxidized at a closely controlled temperature (Figure 1). The sample size was limited to one gram, as a size small enough to explode with safety and still give enough material for testing. The samples of methyl oleate were weighed out into glass-stoppered vials; where a catalyst was used, it was added in a methyl alcohol solution just before oxidizing. The sample was then dispersed on glass wool by injecting it into the glass wool plug (Figure 1) with a hypodermic syringe. This gave fairly good gas-liquid contact, approaching that of a thin film. The glass capsule containing the glass wool was dropped into the pre-heated metal block, the apparatus was assembled, and gas pressure was applied. Gross heating was supplied through a bath of hydrogenated tallow; close temperature-control was maintained by a thermocouple-controlled resistance winding directly on the metal block. At the end of the reaction the glass tube was removed from the vessel and centrifuged to remove the oxidized sample from the glass wool. The peroxide value was determined by the
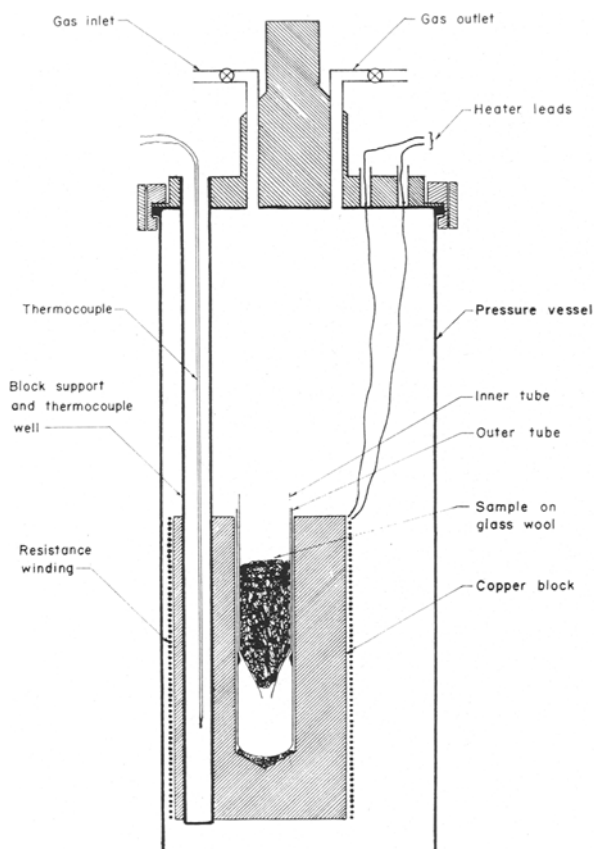
FIG. 1. Reaction vessel used for pressure reactions.

Wheeler iodometric procedure, using a sample of about 0.2 g. The acidity was determined on about 0.1 g. of the material, dissolved in neutral methyl alcohol, by titrating with 0.05 N KOH to the phenol red end-point.

### Results

Figure 2 shows the magnitude of the effect of increased pressure on the peroxide at 120°C. A pressure of 800 p.s.i.a. (pounds per square inch absolute)
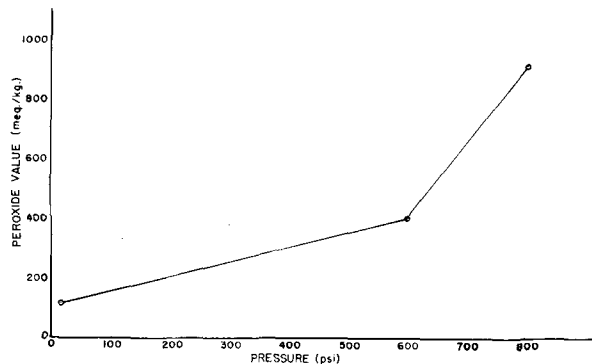


FIG. 2. Effect of pressure on the peroxide value of methyl oleate autoxidized for 0.5 hr. at 120°C.

$O_2$ increased the PV (peroxide value) to about 10 times the value produced at atmospheric pressure. A calculated yield of approximately 16% was ob-

tained after 0.5 hrs. at this pressure. Higher pressures, or longer reaction-times, resulted in explosions at this temperature. This effect is illustrated in Figure 3. At atmospheric pressure the shape of the
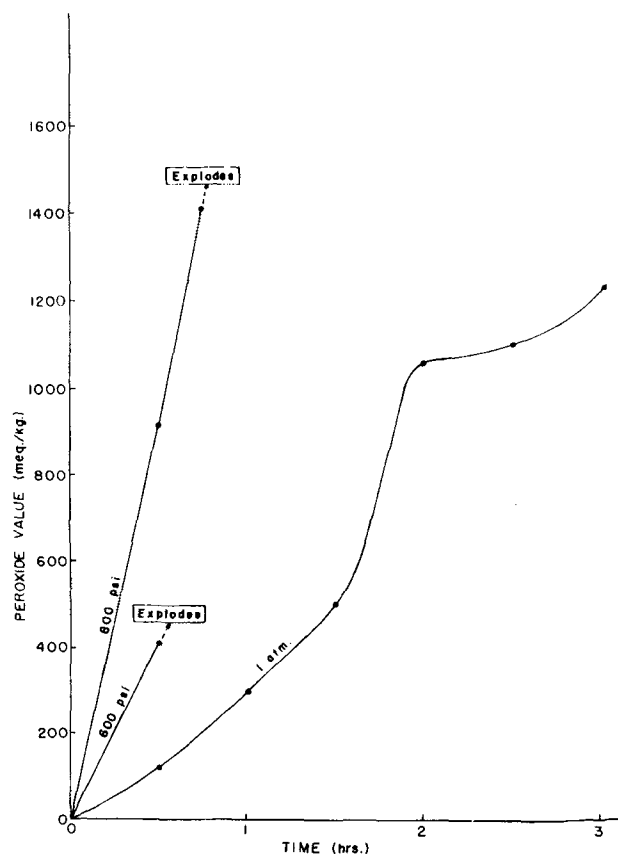


FIG. 3. Effect of pressure on the peroxide value of methyl oleate autoxidized at 120°C.

time-PV curve is that typical of autoxidation reactions. Under pressure the induction period, if present at all, is very short. At 800 p.s.i.a. $O_2$ a PV of 1,410 (23%) was obtained after ¾ hr. At this temperature however the reaction was unpredictable at either pressure used, if extended beyond ½ hr. A series of oxidations at 100°C. was carried out by using a variety of oxygen pressures. In Figure 4 the PV curves are compared with that at atmospheric pressure. None of the samples exploded. The shapes of the curves are somewhat similar; the principal effect of increased pressure is that of encouraging earlier peroxide decomposition. A comparison of the results at 120° and 100°C. suggests that different types of reaction may occur at the two temperatures. Figure 5 shows the effect of pressure in increasing the formation of acids in the same samples. Eight hours at 800 p.s.i.a. $O_2$ gave a sample containing 1,350 meq./kg. of titratable acid, a calculated yield of about 24%.

The catalytic effect of heavy-metal, multivalent metal salts was of interest not only because of the effect in promoting secondary oxidation,. raising the acid yield, but also because of the possibility of preventing explosions by limiting the level of hydroperoxides present at any one time. Assuming that the explosions were caused by a spontaneous decomposition of hydroperoxides, a catalyst that decomposes
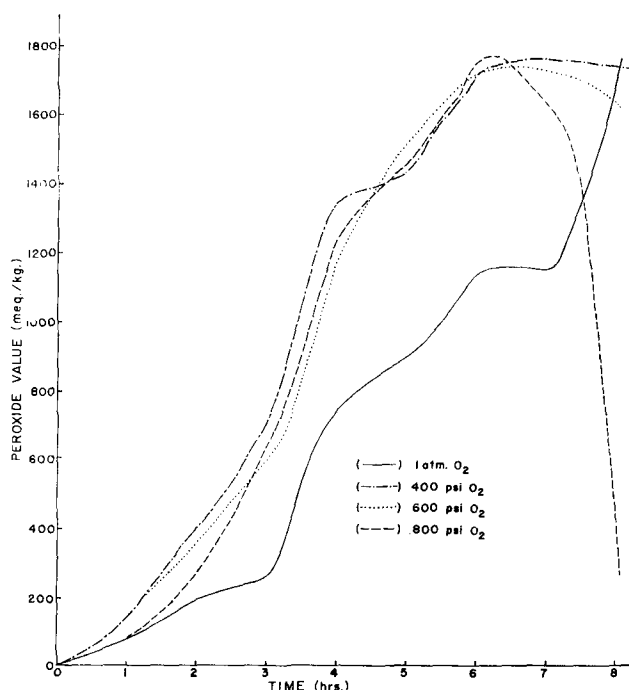
FIG. 4. Effect of pressure on the peroxide value of methyl oleate autoxidized at 100°C.

creased with increasing pressure, up to 200 p.s.i.a. $O_2$. Above this pressure the reaction exploded.

In the system being used both pressure and catalyst had definite limits in their capacity to increase peroxide yields. Acidity however could continue to increase so long as pressure, temperature, and cata-



FIG. 6. Effect of catalyst concentration on the peroxide value and titratable acidity of autoxidizing methyl oleate. Pressure, 200 p.s.i.a. $O_2$; temperature, 100°C.; time, 1 hr.

hydroperoxides would perhaps prevent the accumulation of an explosive concentration. Using cobalt acetate as the catalyst, the explosiveness of the reaction was increased rather than diminished. At 100°C., in the absence of catalyst, the reaction was stable up to 800 p.s.i.a. At the same temperature (Figure 6), under only 200 p.s.i.a. $O_2$, the presence of more than 0.003% cobalt acetate caused the sample to explode in less than 1 hr. Below this concentration both peroxide value and acidity (Figure 6) increased with the increasing catalyst concentration. Again, at 100°C., 1-hr. reaction time and 0.002% cobalt acetate, the peroxide value and the acidity (Figure 7) in-
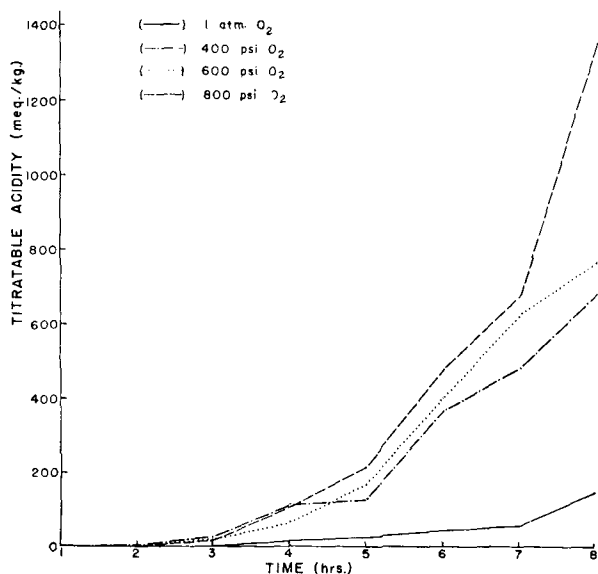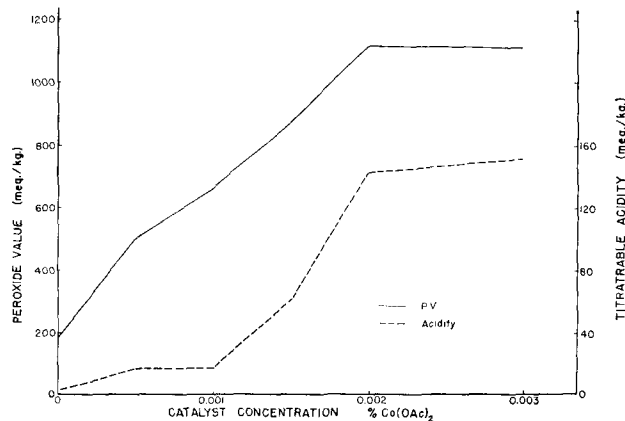
lyst were kept below the critical limits. Using air at a pressure of 100 p.s.i.a., 0.1% cobalt acetate, and a temperature of 100°C., a series of methyl oleate samples were oxidized for increasing periods of time. Figure 8 shows the quite high acidities that can be
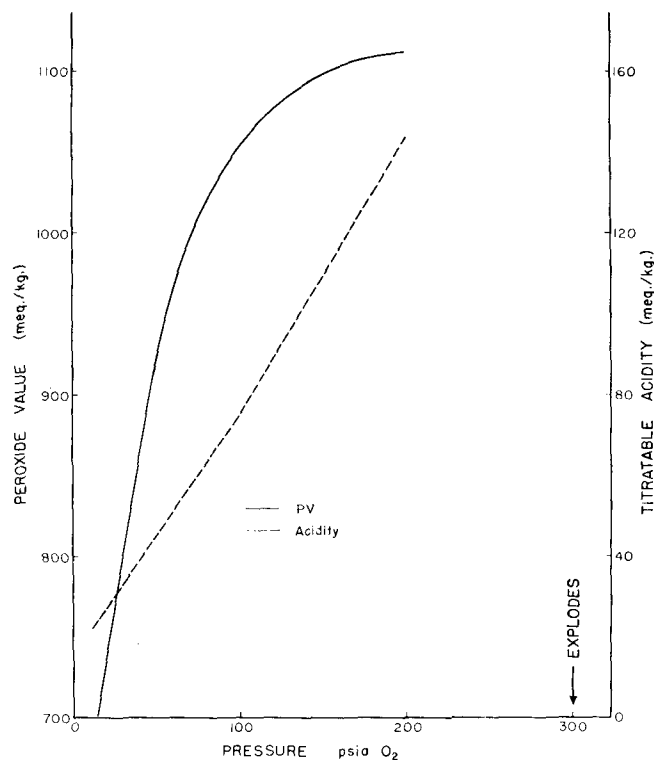


FIG. 5. Effect of pressure on the titratable acidity of methyl oleate autoxidized at 100°C.



FIG. 7. Effect of pressure on the peroxide value and titratable acidity of autoxidizing methyl oleate. Catalyst concentration, 0.002% Co (OAc)$_2$; temperature, 100°C.; time, 1 hr.
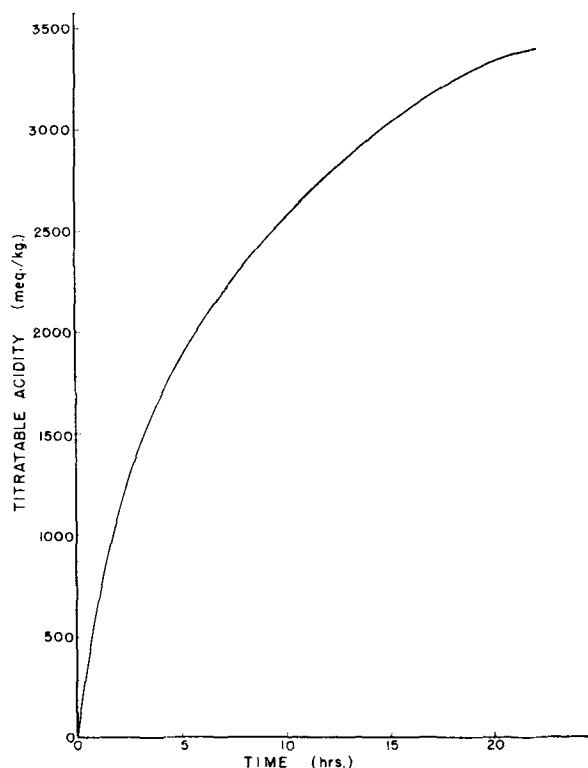
FIG. 8. Effect of increasing reaction time on the titratable acidity of autoxidizing methyl oleate. Catalyst concentration, 0.1% Co(OAc)₂; pressure, 100 p.s.i.a. air; temperature, 100°C.

built up if the reaction is continued long enough. After 22 hrs. about 3,400 meq./kg. of titratable acid was present in the oxidized oleate.

### Discussion

The explosions were apparently caused by an accelerated oxidation of the liquid phase rather than by the reaction of gaseous by-products with $O_2$. In all explosions the liquid sample itself exploded, shattering the glass capsule; in some, mild combustion caused the glass wool to melt. In one experiment the explosion occurred as soon as the pressure was applied; thus a reaction due to by-product oxidation is ruled out unless it occurred extremely fast. It is possible that oxidative products, such as hydroperoxides, were built up in the samples until some critical concentration was reached, resulting in an explosion. It is also possible that the reaction involves a direct union of $O_2$ with the unsaturated linkage, suggested by Gunstone and Hilditch (5) as the initiating reaction in forming hydroperoxides. The method of carrying out the oxidation doubtless has a significant effect on the course of the reaction. In this work the oleate was essentially in the form of a thin film. Bulk oxidation, using a gas disperser, would perhaps give better yields, but the present state of our knowledge does not permit the extension of pressure oxidation to larger batches with any assurance that they would not explode.

Product analysis, which may throw some light on the peculiarities of pressure oxidation of unsaturated esters, has not been completed. The pressure oxidation of oleic acid is said to give a high yield of lactones (4). The oxidized methyl oleate reacts with neutral hydroxylamine to form hydroxamic acids, a reaction characteristic of both lactones and peresters (3). At the temperatures used some interesterification may take place to produce lactones from hydroxyesters, but peresters are equally likely.

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# Melting and Dilatometric Behavior of 2-Oleopalmitostearin and 2-Oleodistearin[1]

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The glycerides, 2-oleopalmitostearin and 2-oleodistearin, which are important components of confectionery fats, were synthesized, and their melting behavior and dilatometric properties were determined.

Each glyceride was found to have four melting points: 18.2, 24.5, 33.0, and 37.4°C. for 2-oleopalmitostearin; 22.8, 30.0, 37.7, and 42.8°C. for 2-oleodistearin. The rate of transformation of the thermodynamically unstable polymorphs at temperatures just below their melting points was found to vary from a few seconds to more than eight days.

For each glyceride, expansivities were determined for three polymorphs and melting dilations for two polymorphs. Mixtures of the two glycerides were examined dilatometrically and found to behave in some respects as single components. The mixtures were readily tempered so that both components were in the same polymorphic form, and expansivities and melting dilations were obtained for mixtures in three polymorphic forms.

Dilatometric data also were obtained for a sample of cocoa butter and a sample of sweet milk chocolate of the coating type.

ON THE BASIS of both direct and indirect proof the triglycerides, 2-oleopalmitostearin and 2-oleodistearin, comprise about 75% of cocoa butter. Several investigators (1,11,17) have found that cocoa butter contains a large proportion of oleopalmitostearin, up to 57%; and recently conclusive evidence