The Mechanism of Cobalt Drier Action

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Abstract

The influence of cobalt driers on the initial stages of the drying of polyunsaturated esters has been studied. Cobalt (II) appears to form an unstable complex of variable composition with the polyunsaturated ester. This complex catalyzes the uptake of oxygen and increases the rate of oxygen absorption by the ester. The energy of activation for oxygen uptake by the ester in the presence of cobalt is only 1.3 kcal/mole, while in the absence of cobalt, the activation energy is 10.8 kcal/mole. The absorption of oxygen by the ester is followed by the formation of hydroxy and/or hydroperoxy groups, the loss of alkene groups, an increase in conjugation and conversion from the cis to the trans isomer. Polymerization occurs during these latter changes.

Introduction

POLYUNSATURATED ESTERS absorb oxygen and undergo free-radical initiated polymerization to form "cured" films. After an induction period, the sequence of oxygen absorption, peroxide formation, peroxide decompostion and polymerization takes place. The viscosity of the oils begins to increase as the peroxide decomposes and the molecular size increases. This series of transformations, extensively studied by many investigators, has been thoroughly reviewed by Mueller (1).

Drier metals, such as cobalt, accelerate these changes by shortening the induction period, increasing the rate of peroxide formation, peroxide decomposition, and polymerization. While the effect of the drier is known, the mechanism of the catalysis is not thoroughly understood. Proposals include:

(a) Deactivation of natural antioxidants in the oil by the drier metal.
(b) Driers accelerate oxygen absorption by catalytic action.
(c) Driers react with oxygen to form a compound which reacts with the double bonds of the oil. Oxygen is given up, and the cobalt liberated to react further with oxygen.
(d) Driers combine with the drying oil at the double bond forming a compound which reacts with oxygen.

Mueller (1) proposes the generation of a free carboxyl radical from the metal salt, which abstracts H from an α-methylenic carbon atom, starting a chain reaction. The activated double bond combines with oxygen free radicals and forms peroxides. The peroxides are decomposed by Co^{++} as follows:

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

Polymerization subsequently occurs.

The objective of this work was to investigate the nature of drying oil-drier metal interactions which occur before and during the ultimate polymerization sequences.

Experimental

Apparatus and Reagents

A Beckman Model DU spectrophotometer was used for the measurement of absorption spectra in the visible and ultraviolet regions of the spectrum. A Perkin-Elmer "Infracord" employing sodium chloride optics was used in the early stages of this work for measurements in the infrared region but in the later work, a Perkin-Elmer Model 21 spectrophotometer with lithium fluoride optics was used.

A Sargent Model XV recording polarograph was employed for the polarographic studies.

The apparatus for the study of oxygen uptake is shown in Figure 1. The all-glass apparatus was connected through stopcocks and a "T" tube to a vacuum pump (B) and to a tank of oxygen (A). This portion of the assembly was used to evacuate the apparatus, sweep with oxygen and to admit oxygen to the gas buret when needed. A standard taper 10/30 joint (D) connected the reaction-vessel assembly (E and F) to the rest of the apparatus. A gas buret (G) of 10 ml capacity and calibrated to 0.05 ml was connected to a leveling bulb (I) filled with mercury and to a fine-capillary manometer (H) containing dibutyl phthalate.

Conjugated Methyl Linoleate. Six hundred grams of linoleic acid (Baker's 9-11 acids; 93% linoleic acid, 30% conjugated double bonds, acid number 197, saponification equivalent 198, iodine number 153) and 640 g of methanol were placed in a three-necked flask which was fitted with a stirrer, nitrogen inlet tube and thermometer, and a condenser and water trap. Five milliliters of 5 N hydrochloric acid were added as a catalyst. The reaction was allowed to proceed at reflux for a period of about 10 hr. Several samples were removed at intervals during the reflux and the acid number of each sample was determined. An additional 300 ml of methanol was added during the heating period. When the acid number of a sample of the refluxing mixture was 6.4, the heating was stopped. The contents of the reaction flask were dissolved in 500 ml of petroleum ether and this solution was extracted 5 times with 100-ml portions of 70% alcohol containing 5% sodium hydroxide and was then washed several times with distilled water. The ether fraction was allowed to stand for a day over anhydrous sodium sulfate and under a nitrogen atmosphere. The solution was then filtered, while a nitrogen atmosphere was maintained over the solution. The ether was distilled under reduced pressure. The resulting crude ester was then heated under a nitrogen atmosphere to 155C for 30 min to remove any peroxides or volatile components. The final product had a peroxide value less than 0.02%, a negligible acid number, an iodine number of 143 and a saponification equivalent of 199. By

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ultraviolet absorption, the ester contained 35% conjugated double bonds.

Pure Unconjugated Methyl Linoleate. This ester, obtained from the Hormel Foundation, University of Minnesota, Austin, Minnesota, was prepared by urea-complex formation of safflower seed oil, low temperature fractional crystallization and high-vacuum distillation. The purity estimated by gas-liquid and paper chromatography was greater than 99%. The iodine value was 172, the diene conjugation 0.3% and the peroxide value negligible.

Cobalt Octoate Drier. One mole (144.3 g) of 2-ethylhexanoic acid (Union Carbide) was added with agitation at room temperature to 188 g (1 mole) of 21.3% aqueous sodium hydroxide to form one mole of sodium 2-ethylhexanoate. After the mixture was uniform, 15 g or approximately 10% excess acid was added, followed by the addition of 300 g of C.P. isooctane.

This was followed by the dropwise addition of 402 g (0.5 moles) of a 35% aqueous solution of reagent grade $CoSO_4.7H_2O$. An additional 12 g or 3% excess cobalt sulfate solution was added to insure complete reaction. The reaction mixture was then placed in a separatory funnel, allowed to separate, and the lower aqueous layer containing the excess cobalt sulfate and by-product sodium sulfate were drawn off and discarded.

The upper layer containing the cobalt soap was transferred to a 3-necked round-bottom flask equipped with an agitator, reflux condenser and water trap. This drier solution was refluxed at atmospheric pressure until all the water was collected in the trap. It was then filtered with the aid of Celite 503 and after analysis, the filtrate was reduced to 6% cobalt by weight with isooctane.

Procedures

A. *Visible and Ultraviolet Spectrophotometric Analysis.* Most measurements in this region of the spectrum were made on isooctane solutions of methyl linoleate with known amounts of cobalt drier added. The change in the absorbance of these solutions was determined as a function of age in the presence or absence of oxygen and/or light.

The diene conjugation was determined spectrophotometrically according to the method described in the American Oil Chemists Society-Official Method Cd 7-58. A known concentration of diene was prepared in isooctane and the absorbance of this solution was measured at 2330 A. The diene conjugation was calculated from the relation:

Percent Diene Conjugation =

$$\left[\frac{\text{Absorbance}}{C \times G} - 0.07 \right] 0.91$$

C = Cell length in cm.
G = g/l of diene

For the slope-ratio method (2) to determine the number of methyl linoleate molecules associated with each cobalt ion, two series of solutions of methyl linoleate and cobalt drier were prepared. In the first series, the concentration of the cobalt was held constant at 4 x 10^{-3} M and the methyl linoleate was varied from 1 x 10^{-5} to 4 x 10^{-5} M. In the second series, the conditions were reversed in that the methyl linoleate was held constant at the higher concentration and the cobalt concentration was varied. The absorbance of all of these solutions was measured between 2550 and 3000 A.

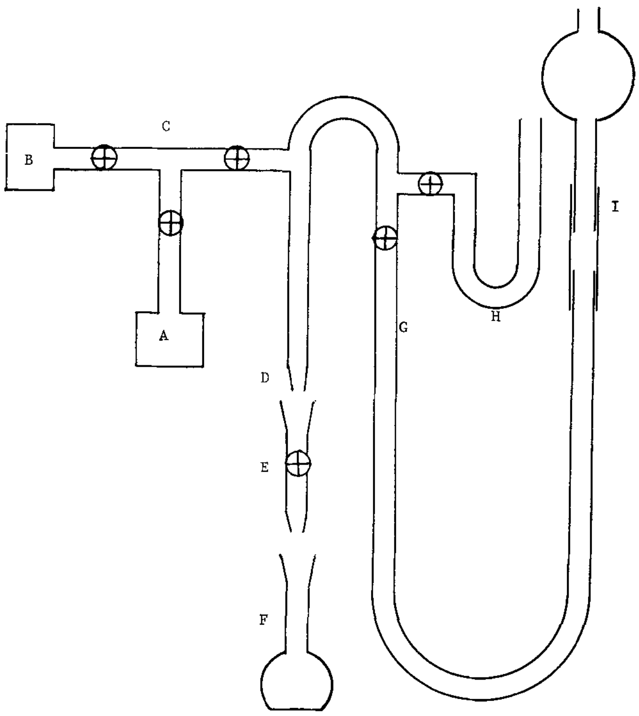

FIG. 1. Oxygen uptake apparatus.

B. *Infrared Spectroscopy.* Infrared absorption curves were recorded generally from 0.025 mm thick films of the methyl linoleate placed directly on the sodium chloride windows. The effect of aging on the infrared spectrum of these films with or without cobalt present, with or without ultraviolet radiation, and in the presence or absence of oxygen was determined.

In order to eliminate the effect of intermolecular bonding, some infrared absorption curves were recorded between 2.5 and 4.0 μ using very dilute solutions (0.1% by volume) of methyl linoleate in carbon tetrachloride in 1 cm silica cells.

C. *Enthalpy Titrations.* A solution of 4.5 to 5.0

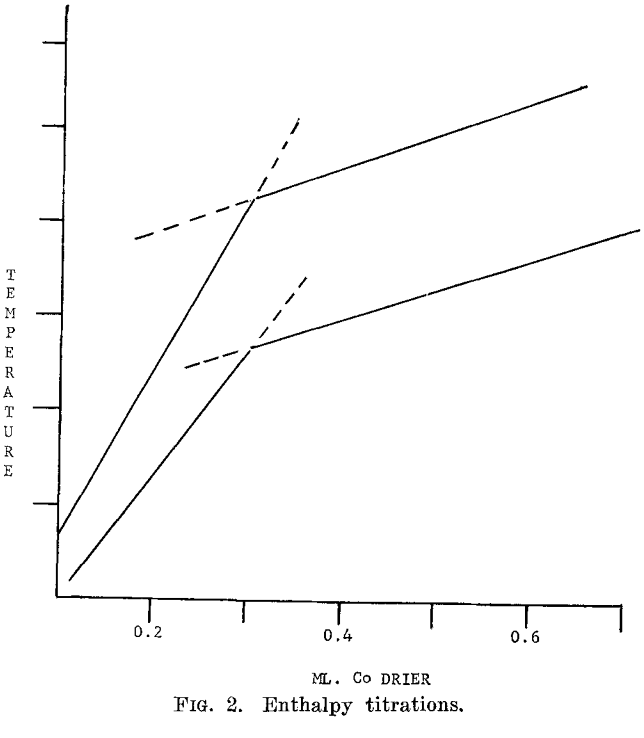

FIG. 2. Enthalpy titrations.

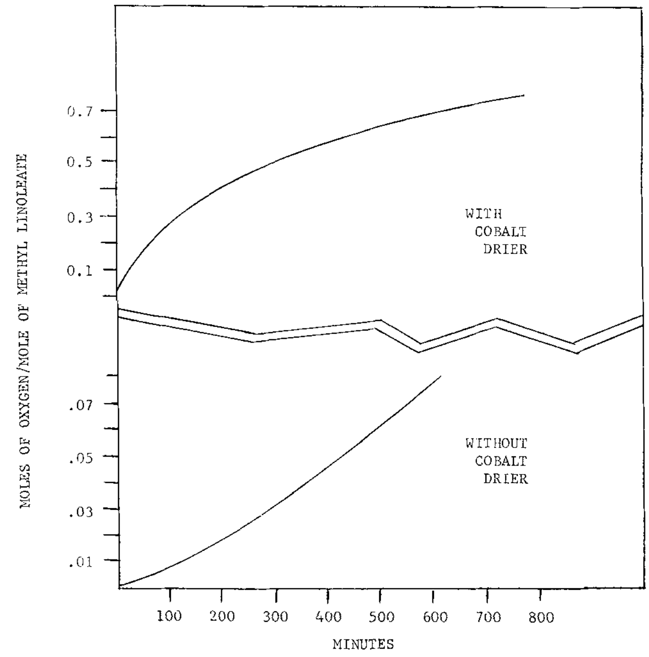

FIG. 3. Oxygen uptake of pure methyl linoleate.

ml of pure unconjugated methyl linoleate in 47 ml of isooctane was placed in a beaker. The temperature of this solution was measured while small increments (0.05 ml) of 6% cobalt drier were added. The rise in temperature was then plotted vs. the volume of cobalt drier added.

D. *Oxygen Uptake.* Approximately 0.5 g portions of methyl linoleate were weighed carefully under a nitrogen atmosphere into the reaction vessel shown in Figure 1. This vessel contained a small magnetic stirring bar and a glass bead. In the experiments employing cobalt drier, a 10 μ portion of the 6% cobalt octoate was sealed into a small fragile glass vial and also placed in the reaction vessel. (This amount of drier provided a concentration of cobalt equivalent to 0.1% by weight of the ester.) After the stopcock section was attached to the reaction vessel, the latter was evacuated. This assembly was connected to the apparatus which, with the exception of the reaction vessel, was alternately evacuated and filled with oxygen. The reaction vessel was left to equilibrate in a constant temperature bath (±0.3C). After the apparatus was filled with oxygen, the magnetic stirrer under the reaction vessel was turned on and oxygen was admitted to the evacuated reaction vessel. The volume of oxygen at atmospheric pressure in the gas buret, atmospheric pressure, and the temperature of the apparatus were measured. At timed intervals these measurements were repeated. The resulting gas volumes were reduced to standard conditions and then calculated as the volume of oxygen absorbed. The rate of oxygen absorbed was plotted as a function of the moles of oxygen absorbed/mole of ester vs. time.

The experiments were conducted at 25C, 35C and 45C and also for various lengths of time. At the end of each experiment, a sample of the ester was removed, diluted with isooctane to a concentration of 0.02 g to 0.2 g/liter and the per cent of diene conjugation was determined from spectrophotometric measurements.

The magnetic stirring bar and the glass bead in the reaction vessel serve to agitate the contents of the flask and to fracture the glass vial containing the drier. Thus, it is possible to mix the ester and drier at a definite time and observe the rate of oxygen absorbed in the early stages of the drying process.

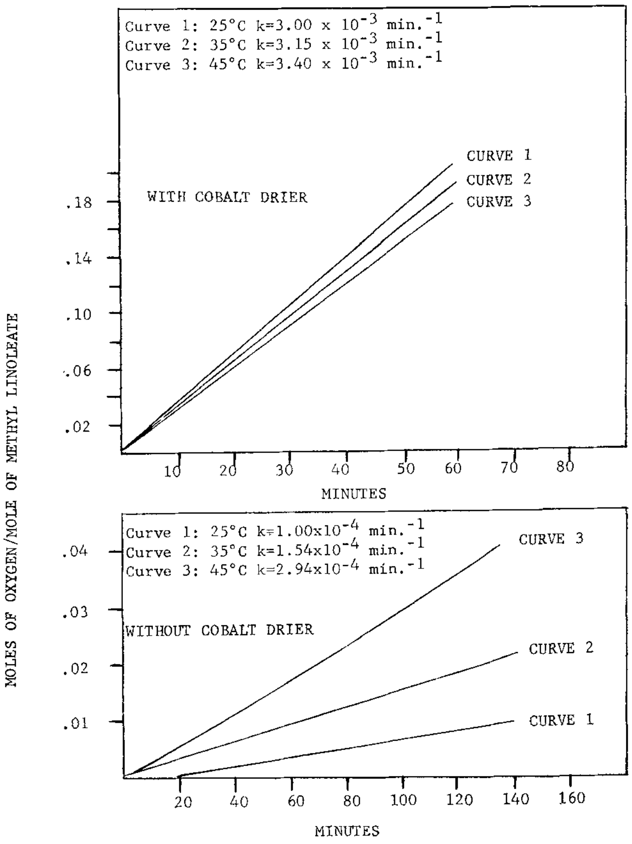

FIG. 4. Rate constants for unconjugated methyl linoleate.

E. *Polarographic Analysis.* Solutions of cobalt octoate and methyl linoleate were prepared in methanol containing 0.2 *M* sodium perchlorate and in a medium composed of 324 g of ammonium acetate, 210 ml of ethylene glycol, 420 ml of heptane, 3360 ml of isopropyl alcohol, 240 ml of water and sufficient glacial acetic acid to make one half the volume of the previously mixed components. The polarographic behavior of these solutions was investigated in standard "H" type cells between 0 and - 2 volts versus a saturated calomel reference electrode. The effect of aging these solutions under a nitrogen or oxygen atmosphere was followed by periodic measurements.

Discussion

When cobalt salts are added to drying oils, the initial blue color changes rapidly to yellow-green. The same color change occurs when cobalt drier is added to pure methyl linoleate. Experimental evidence indicates that Co^{++} form a transient complex of low energy content with the π electrons of the polyene. Complex formation is followed by isomerization to the conjugated state, transition from the cis to trans configuration, and a comparatively rapid rate of oxygen absorption. Evidence supporting these conclusions was derived from visible, ultraviolet, and infrared spectrophotometry, enthalpy titrations, measurement of oxygen absorption, polarography, and determination of activation energy.

Loss of the cobalt absorption peak at 5830 A and a bathochromic shift indicate a chemical association between methyl linoleate and cobalt. The observation was made using solutions containing (1) 100 g of methyl linoleate (0.3% conjugated double bonds,

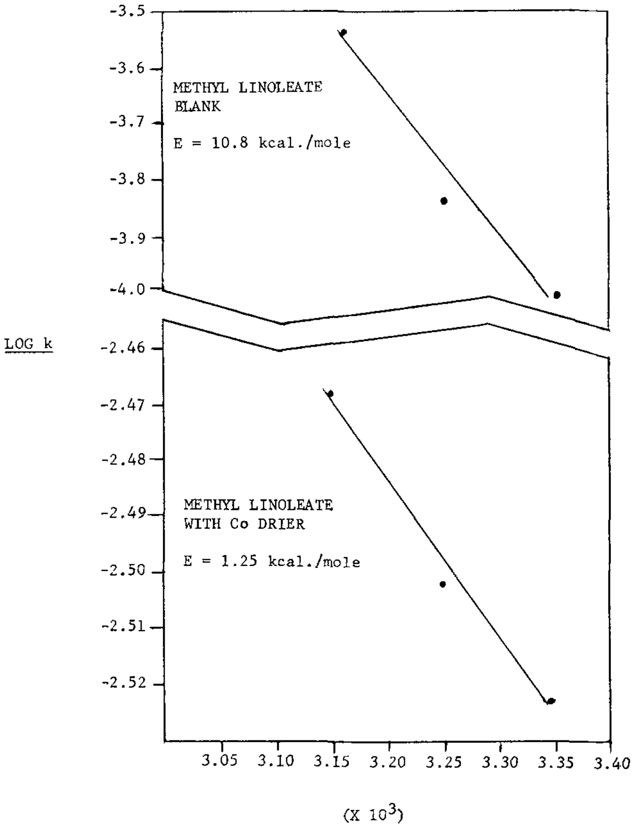

FIG. 5. Log of rate constants vs. 1/T.

100% cis configuration), 0.1% of cobalt per liter of isooctane; (2) 100 g of methyl linoleate (35% conjugated double bonds, cis-trans ratio unknown). While the same color change occurred in both solutions, a significant rate difference was noted. The color change of the pure ester solution was almost immediate. Equal change in the conjugated ester solution required several days. The direct photometric titration of methyl linoleate with cobalt octoate, and the slope-ratio technique (2) indicate that a weakly bonded complex of 8 to 12 moles of methyl linoleate per mole of cobalt is formed.

Data from infrared spectra indicate that cobalt accelerates the changes that occur in methyl linoleate during its exposure to air without altering significantly their nature. The unconjugated methyl linoleate containing 0.1% cobalt drier shows three absorption bands between 2.5 and 4.0 μ. Resolution of these bands with a LiF prism shows a sharp band at 3.3 μ, a broad one at 3.43 μ, and a sharp one at 3.51 μ. When a 0.25 mm film, on a sodium chloride window, is exposed to the air, a broad band between 2.84 and 9.9 μ develops rapidly, changing from 100% transmission to 60% transmission in 6 hr but then reaches a steady value at 30% transmission after several days. In addition, the sharp band at 3.33 μ becomes less distinct with time of exposure of the methyl linoleate to air and after 10 days has disappeared. At the same time, the absorption bands at 3.43 and 3.51 μ increase. On the other hand, the same methyl linoleate without cobalt drier but maintained under an identical environment develops a sharp band at 2.93 μ but does not lose the absorption at 3.33 μ.

Methyl linoleate containing cobalt drier shows a small increase in absorption at 5.82 μ and a much greater increase at 6.15 μ with time. Also, a distinct band at 10.3 μ as well as less distinct bands at 9.0 and 9.85 μ develop with time. Methyl linoleate without drier shows essentially these same changes but merely at a much slower rate.

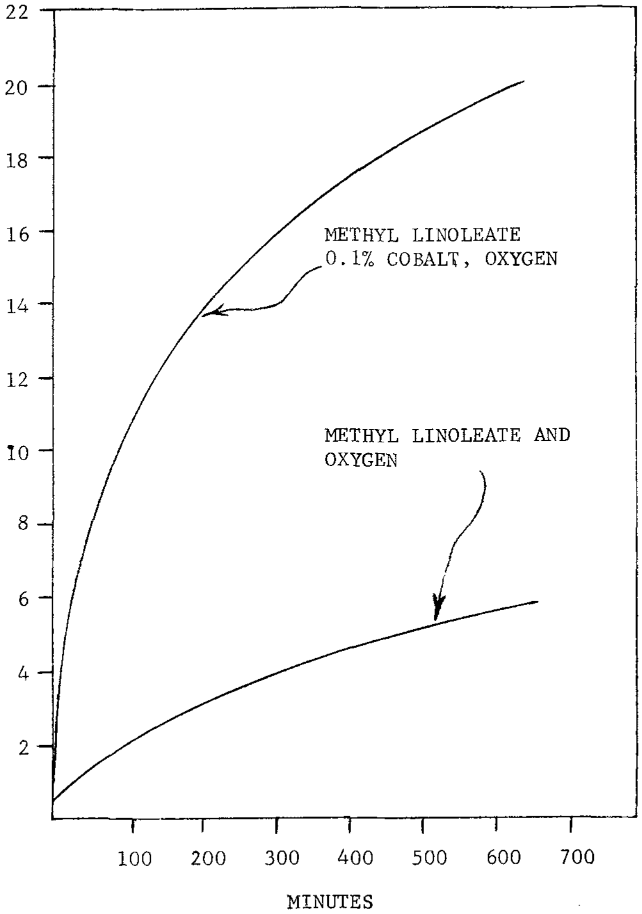

FIG. 6. Oxygen-induced conjugation in unconjugated methyl linoleate at 25C.

The rapid appearance of the band at 2.84 - 2.94 μ suggests that OH and/or OOH bonds are formed rapidly in methyl linoleate containing cobalt drier. The intensity of this band appears to reach a steady state after several days of standing. Therefore, the formation of hydroxyl and/or hydroperoxy groups must cease or else be consumed as rapidly as generated. The latter alternative seems to be more plausible because the spectra at higher wavelengths continue to show significant changes after the steady state at 2.84 - 2.94 μ is reached.

The loss of olefinic groups in methyl linoleate during its aging can probably be correlated with the decrease and disappearance of the alkene band at 3.33 μ. The other major absorption at 10.3 μ that intensifies with time is undoubtedly due to the formation of the trans isomer. These two phenomena have been reported by previous workers (3-6) and are included here merely to emphasize that methyl linoleate undergoes the same conversions as the more typical drying oils.

The heat of formation of the complex formed with the drier and ester was determined by thermometric titrations. The experiments were conducted in a cell which contained methyl linoleate in 47 ml of isooctane and with samples of 4.5 ml and 5.0 ml, respectively, of ester. The solutions were stirred and small increments of cobalt octoate were then added. The rise in temperature of the solutions for each cobalt addition was noted and a plot was made of temperature vs. volume of cobalt octoate added (Fig. 2). Two slopes were observed for each experiment. The Δ H for the

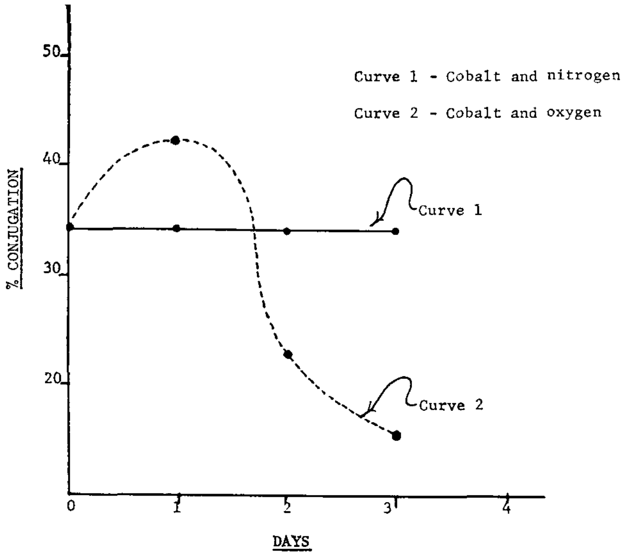

FIG. 7. Change in composition of conjugated methyl linoleate.

reaction at the intersection of these two slopes was calculated from the weight of methyl linoleate, the volume and heat capacity of isooctane, the volume of cobalt octoate and the temperature change.

The average value for △ H at the intersection of the two slopes obtained from the two enthalpy titrations is 20 kcal/mole of cobalt added. This value for the △ H is for a complex that appears to have 1 mole of cobalt to 100 moles of methyl linoleate.

The titration curves in Figure 2 suggest that two different types of cobalt complexes are formed with methyl linoleate. The first is considerably more stable and more exothermic than the second as evidenced by the greater slope during the initial addition of cobalt. It is likely that continued addition of cobalt would have eventually produced a solution that would show no further temperature changes with cobalt added. It is also possible that this point where no further heat would be generated with addition of cobalt would occur at an approximate mole ratio of cobalt to methyl linoleate of 1:10.

In the absence of cobalt, purified methyl linoleate containing 0.3% of conjugated double bonds absorbed oxygen very slowly during a 75 min induction period. After this period, the rate of absorption increased and became nearly a linear function with time. A total of 0.085 moles of oxygen per mole of ester was consumed during an 11 hr period. When the same experiment was conducted in the presence of 0.1% of cobalt, the induction period was eliminated. The oxygen consumed during an 11 hr period was 0.740 moles per mole of ester (Fig. 3).

The rate of uptake of oxygen by methyl linoleate in the presence and absence of cobalt was measured at 25C, 35C and 45C. The rate constants for the reaction of the pure unconjugated ester with oxygen at the three temperatures for runs of 2-1/2 hr duration was determined. The data and rate constants are shown in Figure 4.

The logarithms of the rate constants for the ester and ester-drier systems vs. the reciprocal of the absolute temperature is plotted in Figure 5 and the activation energy for each of the systems was calculated. In the temperature range studied, the activation energy for the absorption of oxygen by the diene ester alone was 10.8 kcal/mole and for the ester-drier, 1.3 kcal/mole.

The value of 10.8 kcal/mole for the activation energy for the reaction of methyl linoleate with oxygen is in good agreement with the values reported by Bolland (7) for the reaction of oxygen with ethyl linoleate, by Gunstone and Hilditch (8, 9) with methyl linoleate and by Knorre (10) for the autooxidation of lard. Furthermore, the much lower activation energy, 1.3 kcal/mole, for the reaction of oxygen with methyl linoleate in the presence of cobalt drier clearly suggests why cobalt driers enhance the drying rate of drying oils. As additional corroboration of our rate constants, Anderson (11) found that the rate constant for the oxygen uptake by methyl linoleate containing 0.02% by weight cobalt drier at 25C was 2×10^{-3} min $^{-1}$.

Experiments were conducted to show that oxygen alone will sponsor double bond isomerization to the conjugated state. Figure 6 shows that the percentage of conjugation in methyl linoleate increased from 0.3 to 5.8% in 11 hr in the presence of oxygen alone. When cobalt was present, the per cent conjugation increased to 20% during the same period. The rate constant at 25C for oxygen-induced diene conjugation is 1.67 x 10^{-2} min^{-1}. This rate is greater than the corresponding rate of oxygen absorption of the ester in the absence of cobalt, 1.00 x 10^{-4} min^{-1}. However, the rate of cobalt-induced diene conjugation is 1.25 x 10^{-1} min^{-1}, a rate faster than either oxygen-induced conjugation or oxygen absorption. Therefore, cobalt catalyzed diene conjugation is the rate determining step in the uptake of oxygen by the ester.

Parallel experiments were conducted using methyl linoleate containing initially 35% conjugated double bonds. The variation of the per cent conjugation as a function of time is shown in Figure 7. In the presence of oxygen, the conjugated double bond concentration increased sharply, and then decreased to 15% in four days. Precipitation of polymer occurred after one day and coincided with the decrease in conjugated double bond concentration. In the absence of oxygen, however, the conjugated double bond value remained constant, and precipitation did not occur.

The above observations show that cobalt induces not only the isomerization of double bonds to the conjugated form in the presence or absence of oxygen but also increases the rate of oxygen absorption. A steady state value of approximately 15% of conjugated double bonds is achieved in the presence of oxygen. Higher levels were not observed because of polymerization, and therefore a steady state was established. Finally, the presence of oxygen appears to accelerate the rate of conjugation.

Polarographic data were obtained which further substantiate the existence of an unstable cobalt complex with methyl linoleate. Cobalt drier (2 x 10^{-3} M) and methyl linoleate (2 x 10^{-4} M) when stored under nitrogen exhibits only one reduction wave for cobalt (Co^{++}) in both a neutral conducting solvent (methanol + 0.2 *M* $NaClO_4$) at -1.12 v and in an acidic solvent (acetic acid + ammonium acetate) at −1.20 v. When oxygen is bubbled through the acidic solution and then removed with nitrogen, a small transient second wave appears at −0.35 v, the reported half-wave potential for Co^{+++}. The second wave is unstable and completely disappears within a half hour of standing. Because Co^{+++} is very unstable, it was presumably complexed by the methyl linoleate to permit polarographic measurement.

It has been shown (12) that a shift in the half-wave potential of a metal ion in a neutral solvent indicates that complex formation of the ion has occurred. The current investigation shows that a methanol, sodium perchlorate solution of cobalt drier plus methyl linoleate exhibits a very slight shift in the half-wave potential for the cobaltous ion from −1.12 v to −1.14 v. This shift was observed after the solution had been stored for 18 hours under a nitrogen atmosphere, and 2-1/2 hr of oxygen bubbling.

Alternatively, cobalt in the complex with methyl linoleate may be undergoing a rapid shift from the +2 to the +3 state and back again in a typical catalytic manner. That is, oxygen may oxidize cobalt to the +3 state which, in turn, is reduced to the +2 state by the closely associated ester. The half life of cobalt in the +3 state is comparatively short and can be detected only if the concentration of this oxidation state is increased abnormally by bubbling oxygen through the solution.

REFERENCES

1. Mueller, E. R., Ind. Eng. Chem. *46*, 564 (1954).
2. Harvey, A. E., and D. L. Manning, J. Am. Chem. Soc. *72*, 4488 (1950).
3. Adams, K., R. W. Auxier and C. E. Wilson, Official Digest *322*, 669 (1951).
4. Cannon, J. A., K. T. Zilch, S. C. Burket and H. J. Dutton, JAOCS *29*, 447 (1952).
5. Kahn, N. A., Can. J. Chem. *37*, 1029 (1959).
6. Williamson, L. J. A., J. Appl. Chem. *3*, 301 (1953).
7. Bolland, J. L., Proc. Roy. Soc. A *186*, 218 (1946).
8. Gunstone, F. D., and T. P. Hilditch, J. Chem. Soc. 836 (1945).
9. *Ibid*, 1022 (1946).
10. Knorre, D. G., Y. N. Lyaskovskaya and N. M. Emanuel, Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk. 678 (1957).
11. Anderson, B., and P. Nylen, Acta Chemica Scand. *3*, 1077 (1949).
12. Hsiung, Hsiao-shu and G. H. Brown, Am. Chem. Soc., 138th Meeting, New York City (1960).

[Received June 4, 1964—Accepted July 21, 1965]

Preparation of 2-Decyl-2-Hydroxymethyl-1, 3-Propanediol from Dodecanal and from Petroselinic Acid

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Abstract

Dodecanal was reacted with formaldehyde and potassium hydroxide in ethanol and with formaldehyde and calcium oxide in aqueous methanol to give about 30% of the theoretical yield of 2-decyl-2-hydroxymethyl-1,3-propanediol (DHP).

Petroselinic acid was ozonized in methylene chloride, and the ozonide reduced to aldehydes with formic acid and zinc. The methylene chloride solution was emulsified with water and reacted with formaldehyde and potassium hydroxide. A yield of 32% of DHP was isolated.

Pure 5,5,5-trimethylol valeric acid could not be isolated from the reaction mixture of formaldehyde and potassium hydroxide with the mixed aldehydes from petroselinic acid, but a small amount of material was isolated by ion exchange resins which had high infrared absorption for hydroxyl and carboxylic acid and which polymerized on standing.

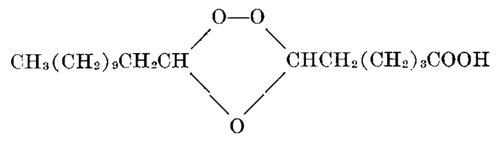
Introduction

AMONG THE OILSEED PLANTS selected for further study in the new crops program of the U. S. department of Agriculture are several members of the Umbelliferae family including parsley (*Petroselinum sp.*),wild carrot (*Daucus carota*), and fennel (*Foeniculum vulgare*). The characteristic fatty acid of the seed oil from these plants is petroselinic (*cis*-6-octadecenoic) acid, and any industrial utilization of the oils would depend primarily on the petroselinic acid or its derivatives.

A derivative that would probably be of much value in the preparation of alkyd resins and plasticizers (1,8,9) is 2-decyl-2-hydroxymethyl-1,3-propanediol (DHP) obtainable by reductive ozonization of petroselinic acid and reaction of the dodecanal with formaldehyde and an alkali.

The reaction of aldehydes with formaldehyde and alkalies is used on a commercial scale to manufacture trimethylol compounds from the shorter chain aldehydes and there is an extensive literature on the preparation and purification of these triols (2,3,4,6,7, 10,11,14). The preparation of DHP from dodecanal or petroselinic acid does not seem to have been reported in the literature. In the reactions involved, formaldehyde condenses with the alpha hydrogens of the longer chain aldehyde to form methylol groups. Another molecule of formaldehyde reacts with the carbonyl group in a crossed Cannizzaro reaction to form a third methylol group. DHP can be formed from petroselinic acid according to the following equations if the ozonization is done in an inactive solvent:

$$\underset{\text{petroselinic acid}}{CH_3(CH_2)_9CH_2CH{=}CHCH_2(CH_2)_3COOH} + O_3 \longrightarrow$$



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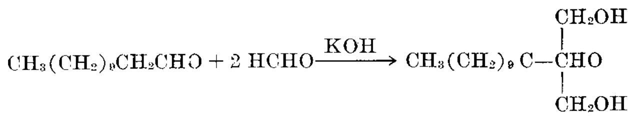
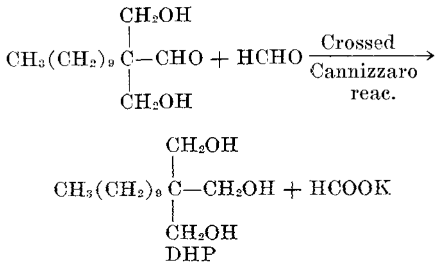
$$\xrightarrow[\text{formic acid}]{\text{zinc}} \underset{\text{dodecanal}}{CH_3(CH_2)_9CH_2CHO} + \underset{\text{adipaldehydic acid}}{OHCCH_2(CH_2)_3COOH}$$

[2]



$$CH_3(CH_2)_9CH_2CHO + 2\,HCHO \xrightarrow{KOH} CH_3(CH_2)_9\,C(CH_2OH)_2{-}CHO$$



[3]

$$CH_3(CH_2)_9\,C(CH_2OH)_2{-}CHO + HCHO \xrightarrow[\text{reac.}]{\text{Crossed}\ \overline{\text{Cannizzaro}}} CH_3(CH_2)_9\,C(CH_2OH)_2{-}CH_2OH + HCOOK$$

DHP

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