The aerobic oxidation of unsaturated fatty acids and their esters: cobalt stearate-catalyzed oxidation of linoleic acid

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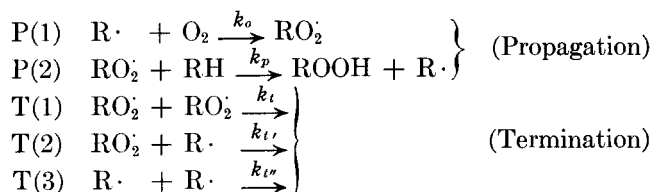
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SUMMARY

The connection between metal catalysis and the initiation step in autoxidation is emphasized. The formation of free radicals occurs in reactions involving not only various valency states, but also oxygen-complexes of the catalyst. The kinetics of the initial phase of the metal-catalyzed aerobic oxidation of linoleic acid are examined in detail, and a number of mechanisms postulated. The rate constants for certain initiation reactions are evaluated together with the corresponding activation energies. The observed values are found to be in fair agreement with theoretical considerations and, in general, the evidence lends further support to the hypothesis that trace-metal catalysis and the initiation of autoxidation are intimately connected.

According to Bateman (1), the interaction of olefins with molecular oxygen is not only a subject of widespread industrial importance but it is also one of the most thoroughly understood chemical processes. However, the difficulties in the understanding of the initiation process were emphasized by one of us recently (2, 3) and are also reviewed in detail in a book (4). The propagation and termination processes of the chain reaction involved in the autoxidation of linoleic acid (5) are generally accepted as:

$$\text{P(1)} \quad \text{R}\cdot + \text{O}_2 \xrightarrow{k_o} \text{RO}_2^{\cdot} \quad \Big\}$$
$$\text{P(2)} \quad \text{RO}_2^{\cdot} + \text{RH} \xrightarrow{k_p} \text{ROOH} + \text{R}\cdot \quad \text{(Propagation)}$$

$$\text{T(1)} \quad \text{RO}_2^{\cdot} + \text{RO}_2^{\cdot} \xrightarrow{k_t} \Big\}$$
$$\text{T(2)} \quad \text{RO}_2^{\cdot} + \text{R}\cdot \xrightarrow{k_{t'}} \quad \text{(Termination)}$$
$$\text{T(3)} \quad \text{R}\cdot + \text{R}\cdot \xrightarrow{k_{t''}} \Big\}$$

Since P(1) is much faster than P(2), $[\text{RO}_2^{\cdot}] \gg [\text{R}\cdot]$ at oxygen saturation, the magnitude of which varies from olefin to olefin. In the case of linoleic acid, the partial pressure of oxygen in air is well above the level required for saturation; hence, as a result of $[\text{RO}_2^{\cdot}] \gg [\text{R}\cdot]$, the only significant termination reaction is T(1).

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On the basis of stationary state kinetics this leads to the rate equation:

$$\text{R(1)} \quad \frac{-d[\text{O}_2]}{dt} = \frac{d[\text{ROOH}]}{dt} = \sqrt{r_i} \times \frac{k_p}{\sqrt{k_t}} \times [\text{RH}],$$

where r_i is the rate of the initiation process leading to the formation of free radicals.

In the presence of peroxide, free radical formation would occur in unimolecular or bimolecular decomposition of the latter, but free radical production prior to peroxide formation has been attributed in most kinetic studies to

$$\text{I(1)} \qquad \text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HO}_2^{\cdot} \quad (5, 6).$$
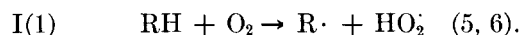
If one accepts the value of ~ -35 kcal as ΔH for the reaction $\text{H} + \text{O}_2 \rightarrow \text{HO}_2^{\cdot}$, in accordance with Evans and Uri (7) and Uri (8), I(1) would be so endothermic that it could not contribute significantly to the initiation process.

Therefore the possibility of the participation of trace metals in the initiation process of autoxidation has been examined, and part of this study is concerned with the elucidation of the mechanism of the catalytic action produced by heavy metal compounds with fatty acids, porphines, and amino acids. Some preliminary results have been previously reported (2, 3). In this paper, which is self-contained as the first of a series, a detailed

account of the mode of action of cobalt stearate is presented.

Some of the complex phenomena observed with cobalt catalysts were described by Bawn (9). In his investigations the importance of the cobaltic state is emphasized, and Bawn's general assumption is that the chain reaction of aerobic oxidation is initiated by an electron transfer reaction between cobaltic ion and either the substrate or its hydroperoxide.

EXPERIMENTAL

Materials Used. Linoleic acid was prepared from tobacco seed oil (rich in linoleic acid) by a procedure involving saponification, urea complex formation with fatty acids, fractional low temperature crystallization, and high vacuum fractionation. Five hundred g of tobacco seed oil (Younghusband, Barnes & Co., London) was dissolved in 500 ml of ethyl alcohol at 60°. Sodium hydroxide (108 g) was dissolved in 400 ml of water, allowed to cool, and added to the alcoholic solution. Saponification is indicated by a substantial rise in temperature and the appearance of a brown-red homogeneous solution. After cooling, aqueous H_2SO_4 (100 ml conc. H_2SO_4 + 400 ml H_2O) was added. The fat layer was separated and washed three times with distilled water. During this whole procedure oxygen-free *nitrogen* was passed through the liquid to prevent aerobic oxidation.

Urea (1.5 kg) was dissolved in 3 liters of boiling redistilled methyl alcohol. With nitrogen bubbling continuously through the liquid, the fatty acids obtained by saponification were added, and after cooling for about 2 hours under nitrogen, the mixture was left overnight at 0°. The precipitated urea complex was filtered under suction, and washed four times with methyl alcohol. Fatty acids were separated by adding the urea complex to 2.75 liters of 2 N hydrochloric acid at 60° to 70°, with nitrogen passing through the solution.

The crude linoleic acid was separated, dissolved in 2 liters of acetone, and left overnight at −35°. Saturated acids were then removed by filtering under suction through a No. 1 sintered glass funnel at −35°. After cooling to −50° and standing for at least 1 hour at this temperature, precipitated monoethenoid acids were removed by filtration at the same temperature. The solution was then kept overnight at −70° and the precipitated linoleic acid was separated by filtration through a Buchner funnel at −70°. Finally, the latter was washed with 100 to 200 ml of acetone cooled to the same temperature.

After removing traces of solvent under vacuum, the colorless, or pale yellow, fatty acid was distilled through a fractionating column under vacuum. The resulting colorless linoleic acid had the following properties: iodine value, 179; acid value, 199; peroxide value, 0.

Methyl linoleate (used sometimes for the purpose of comparison with linoleic acid) was prepared by dissolving 1 volume of linoleic acid in 5 volumes of redistilled methyl alcohol and passing anhydrous hydrogen chloride through the solution, which was cooled externally with ice, until two layers separated. After passing hydrogen chloride for an additional 5 minutes, the liquid was diluted with 10 volumes of distilled water and extracted three times with petroleum ether (b.p. 40°). The time required for esterification was about 15 to 20 minutes and the reaction was at least 99% complete. The combined extracts were washed with distilled water until they were free from acid, dried with anhydrous sodium sulfate, and the solvent evaporated under vacuum. The methyl linoleate was fractionated under vacuum, yielding a colorless product having the following properties: iodine value, 171; acid value, 0; peroxide value, 0.

Cobaltous stearate was prepared by treating 2 volumes of hot (90°) 0.25 M aqueous solution of sodium stearate with 1 volume of cold 0.375 M aqueous solution of cobalt chloride. The mixture was stirred at 70° to 80° for 20 minutes, filtered under suction through a No. 1 sintered glass funnel, and the precipitated cobaltous stearate was washed five times with small quantities of hot (80°) distilled water. The cobaltous stearate was dried in vacuum (≤1 mm) for 2 hours at 75° to 80°.

Analysis: C, 64.5%; H, 11.2%; Co, 9.0%.
Calculated results from $(C_{17}H_{35}COO)_2Co \cdot 2H_2O$: C, 65.4%; H, 11.2%; Co, 8.9%.

The solvent used for studying the oxidation reaction was either benzene (Analar, Hopkin and Williams) or cyclohexane (Howards) purified by shaking with acidified potassium permanganate, passage through a column of activated alumina (Spence, type O), distillation, and finally removal of impurities, particularly aromatic ones, by repeated adsorption on activated silica gel (B.D.H. 30 to 120 mesh) until the extinction measured at 220 mμ in a 1-cm cell against distilled water did not exceed 0.330. All other chemicals used were of Analar quality, B.D.H. or Hopkin and Williams.

For the purpose of tracer work, the following starting materials labeled with radioactive isotopes were obtained from the Radiochemical Centre, Amersham: cobalt chloride—Co^{60} (1.4 mc/mg), stearic acid —1-C^{14} (8.87 μc/mg), and linoleic acid —1-C^{14} (15.8 μc/mg). The linoleic acid was diluted approximately 100 times with carrier material before use. Co^{60}-labeled cobaltous stearate was prepared from labeled cobalt

chloride by the method described above, and after prior neutralization with sodium hydroxide, cobaltous stearate —1-C[14] was prepared from labeled stearic acid by the same procedure.

Methods. In this investigation aerobic oxidation was studied in homogeneous systems, with benzene or cyclohexane as solvent. The solutions were introduced into test tubes (60 ml capacity) stoppered with ground-glass joints, and then shaken in a thermostatically-controlled bath with a specially built-in shaking device. Unless otherwise stated, experiments were carried out at 37° (±0.05°). Solvents were assumed to have reached equilibrium with air, and both the rate of shaking and the liquid surface area to volume ratio had no effect on the rate of reaction in its early stages. The latter factors become significant, however, if solvents are de-aerated prior to their use, or if the reaction is followed to an advanced stage where attention must also be paid to the residual partial pressure of oxygen in the air phase.

Since in the early stages of the aerobic oxidation carbonyl formation is small, the analysis of the reaction mixture was concentrated on direct hydroperoxide determination and measurement of conjugated diene formation (in cyclohexane), allowing a correlation with hydroperoxide formed (further details are given under Results). The direct method of hydroperoxide determination is a modified iodometric standard method and is described by the authors elsewhere (10).

For the purpose of tracer work, Panax Counting Equipment 100C was used in conjunction with a G.E.C. EHM-2S thin end-window Geiger-Muller Counter built into a square lead castle. Counts were carried out in the plateau region of the counter (1500 to 1600 volts) with deadtime paralysis set to 300 μ sec. Thin layers of the material to be counted were produced on standard nickel planchettes by evaporation of the relevant solution with the aid of infrared rays emitted by a lamp mounted above the planchette. Corrections for self-adsorption of C[14] were made by reference to a calibration curve obtained with cobalt stearate (1-C[14]). For Co[60] counts, an aluminium filter of density 900 mg/cm² was used to cut out β-rays.

RESULTS

Correlation Between Hydroperoxide Formation and Conjugation. Lundberg and Chipault (11) reviewed the early findings relating to the formation of conjugated hydroperoxides in diene oxidation. The discovery that there is a parallel occurrence of both hydroperoxide formation and conjugated diene formation was first made in the laboratories of the British Rubber

Producers' Research Association during their fundamental studies of ethyl linoleate autoxidation (12). The literature discrepancies in the evaluation of a molar extinction coefficient of conjugated hydroperoxide derived from various linoleic acid esters are considerable and, to some extent, confusing. These apparently contradictory results, attributing to conjugated hydroperoxide a molar extinction coefficient in the range 22,000 to 32,000, are due to so many factors that their complete analysis is extremely intricate. The principal factors appear to be (a) lack of distinction between oxygen uptake and hydroperoxide formation, (b) insufficient knowledge concerning the stereoisomerism of conjugated hydroperoxide, and (c) the possible formation of a nonconjugated hydroperoxide or secondary reaction products in the relatively early stages of the oxidation.

In view of this complexity, correlation between diene conjugation and hydroperoxide formation is desirable in any special investigation, since it may be frequently affected by choice of experimental conditions; Table 1

TABLE 1. MOLAR EXTINCTION COEFFICIENT OF LINOLEIC ACID HYDROPEROXIDE*

Method of Oxidation	Temperature	(232 mμ, cyclohexane)
Uncatalyzed	25°	28,600
Cobalt stearate catalyzed	25°	29,700
Uncatalyzed	37°	27,900
Cobalt stearate catalyzed	37°	27,300

* Ascertained at peroxide values not exceeding 150.

presents the results of this correlation. The molar extinction coefficient of the linoleic acid hydroperoxide was evaluated at 232 mμ from the optical density of oxidizing linoleic acid in cyclohexane and the iodometric peroxide value, allowing for the absorption of unoxidized linoleic acid of nil peroxide value ($\epsilon = \sim 23$).

The main interest was concentrated on the early stages of oxidation, and there it was found that the correlation between iodometric peroxide value and absorbancy at 232 mμ, as a measure of conjugation, was unaffected by the presence of catalyst; moreover, it remained constant until about 5% of the linoleic acid present was converted into hydroperoxide. Above this level of oxidation there was an apparent progressive drop in the molar extinction coefficient of the hydroperoxide, both in the catalyzed and uncatalyzed oxidations, although this effect was more pronounced in the former.

THE COURSE OF
LINOLEIC ACID OXIDATION

General Observations. Linoleic acid oxidation was first studied in the range of linoleic acid concentrations up to 0.2 M, and cobalt stearate concentrations of 4×10^{-5} M to 2×10^{-4} M in benzene and cyclohexane. Using the technique described in the section on experimental methods to follow the course of the reaction, it was shown that the relationship

$$\frac{d[\text{ROOH}]}{dt} \propto [\text{Linoleic Acid}]$$

(as illustrated in Fig. 1) was obeyed at least as far as a 5% conversion into hydroperoxide. At more advanced stages of oxidation there was a steady increase in the order of reaction rate with regard to linoleic acid, reaching the value of 1.5 at 10% to 15% conversion. The relationship

$$\frac{d[\text{ROOH}]}{dt} \propto [\text{Cobalt Stearate}]$$

(as illustrated in Fig. 2) was obeyed only up to about 1% of hydroperoxide formation. At a higher conversion to hydroperoxide, the order with regard to cobalt stearate decreased, reaching 0.5 at about 3% conversion.
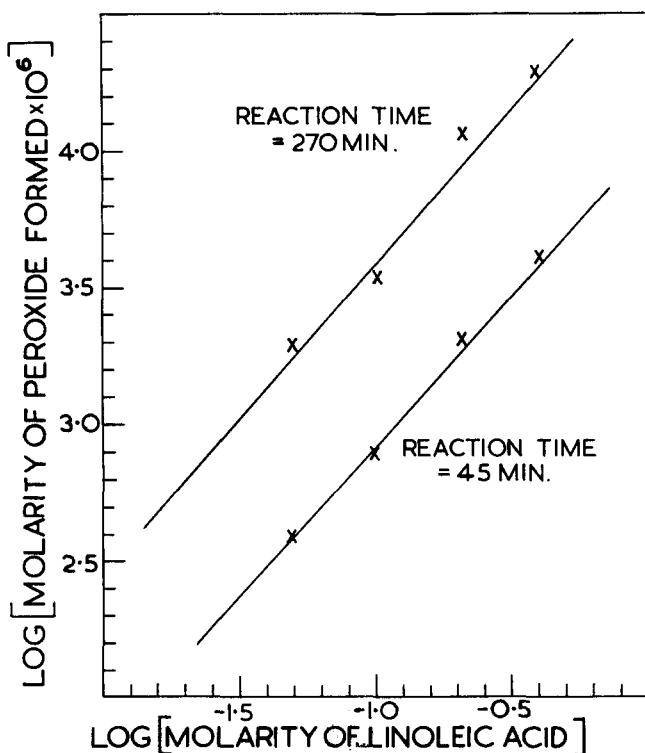
FIG. 1. Effect of linoleic acid concentration on rate of oxidation in cyclohexane at 37°. (Cobaltous stearate concentration = 4×10^{-5} M. Solution saturated with air.)
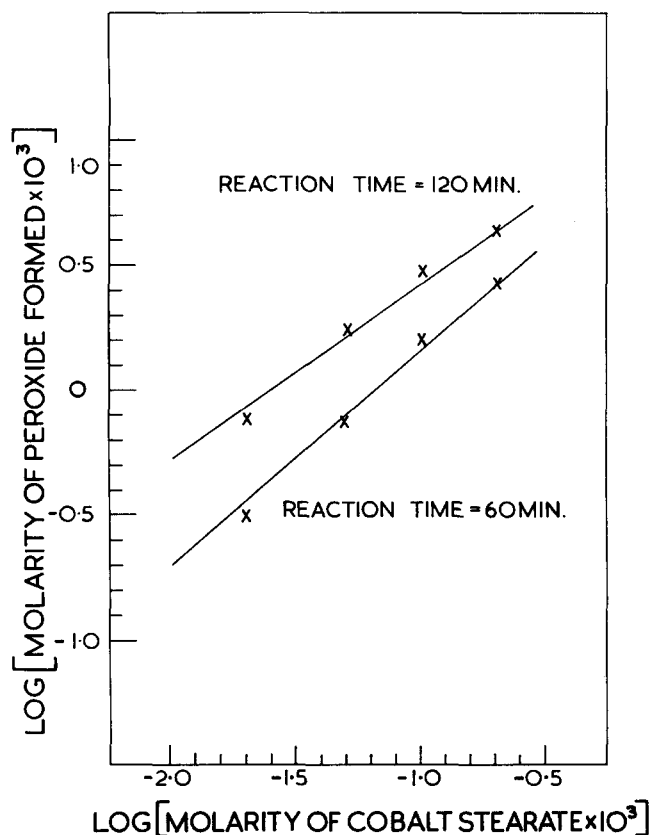

FIG. 2. Effect of cobaltous stearate concentration on rate of linoleic acid oxidation at 37°. (Linoleic acid concentration = 0.1 M. Solvent: benzene.)

Some unusual features were observed when the study was concentrated on the first 0.5% of oxidation at very low concentrations of cobalt stearate ($<4 \times 10^{-5}$ M). The prior equilibrium between solvent and air turned out to be so critical under these experimental conditions that no reliance was placed on the slow establishment of this equilibrium, but solvents containing the catalyst were aerated by bubbling about 10 liters of air through 250 ml of solution; an analogous technique was also employed with all nitrogen-oxygen mixtures used in these experiments. The basic anomaly is illustrated in Figure 3, in which the logarithm of the peroxide value after a fixed time interval (being thus a measure of rate) was plotted against the logarithm of cobalt stearate concentration in order to determine the order of reaction from its slope. The curve obtained was so irregular as to indicate that no simple reaction mechanism could be applied to its interpretation (this is dealt with in detail under Discussion). In view of these anomalous results, the experiment was repeated five times; although slight changes in the absolute value of the rate were observed, dependent on the absolute purity of the batch of linoleic acid employed, the basic phenomenon was found to be strictly reproducible and
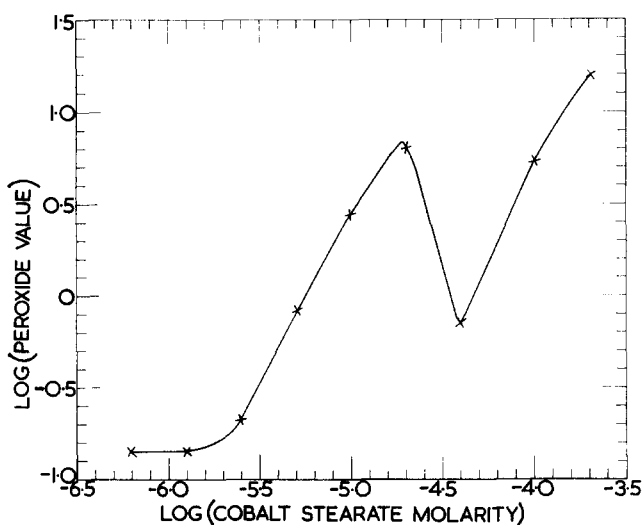
FIG. 3. Reaction order anomaly in the initial phase at low catalyst concentration. (Linoleic acid concentration = 0.1 M. Solvent: cyclohexane. Temperature: 37°. Time of reaction: 30 minutes.) Peroxide value = millimoles peroxide per g linoleic acid.

the maximum always occurred at the same cobalt stearate concentration. However, the critical concentration at which this maximum occurred was shown to be dependent on the temperature and the amount of oxygen in solution. This is illustrated in Figure 4,
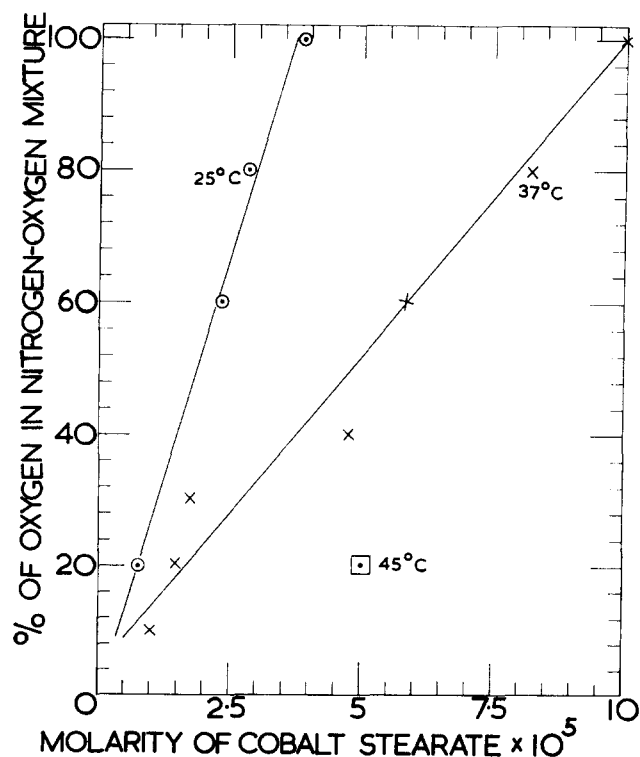

FIG. 4. Effect of temperature and oxygen content on catalyst concentration producing maximum initial rate of oxidation. (Linoleic acid concentration = 0.1 M. Solvent: cyclohexane.)

where the oxygen content was varied by saturating the solvent, in which catalyst had been dissolved, with nitrogen-oxygen mixtures of different composition, prior to linoleic acid addition.

At extremely low cobalt stearate concentrations (e.g., ~2.5 × 10^{-6} M), some departure from the normally observed first-order kinetics with regard to linoleic acid became apparent, but this point was not studied in detail.

Changes in the State of the Catalyst During Oxidation. Cobaltous stearate solutions in benzene or cyclohexane are very pale pink, but for practical purposes no color is discernible with 2 × 10^{-4} M solution in layers 2 cm deep. During oxidation the benzene solution assumes a readily observable yellow color in the range of 0.7% to 1% substrate oxidation. The stable yellow color was measured, and it was shown that the absorbancy of these solutions in the range 350 to 400 mμ was proportional to the original catalyst concentration. There was a steady increase in the absorption coefficient when the wave length was lowered in the above-mentioned region of the spectrum, but it was impossible to ascertain the full spectrum or even an ultraviolet peak because of interference by solvent and oxidized substrate.

When the reaction was carried out in cyclohexane solution, a similar yellow color developed in the same range of substrate oxidation, but this was unstable and its disappearance was accompanied by the formation of a pale yellow precipitate. In order to determine the composition of this precipitate, tracer studies were carried out with Co^{60} and C^{14}. When Co^{60}-labeled cobaltous stearate was used as catalyst, it was found that the precipitate contained 98.5% of the labeled cobalt, which must be regarded as quantitative precipitation within the limits of experimental error. In separate experiments carried out with cobaltous stearate (1-C^{14}) and linoleic acid (1-C^{14}), it was shown that the precipitate contained 0.2 atom of stearate-C^{14} and 2.8 atoms of linoleic acid-C^{14} per atom of cobalt.

Cobaltous-Hydroperoxide Reaction. At cobaltous stearate concentrations up to 10^{-6} M no catalytic effect was observed in the absence of detectable hydroperoxide; the measurements indicated a rate of oxidation which was indistinguishable from the apparently uncatalyzed autoxidation reaction in cyclohexane at linoleic acid concentrations of the order of 0.1 M. Under these conditions a catalytic effect can, however, be observed in the presence of hydroperoxide, and the rate law was established as

$$\frac{d[ROOH]}{dt} \propto [Co^{2+}]^{1/2} [ROOH]^{1/2} [RH]$$
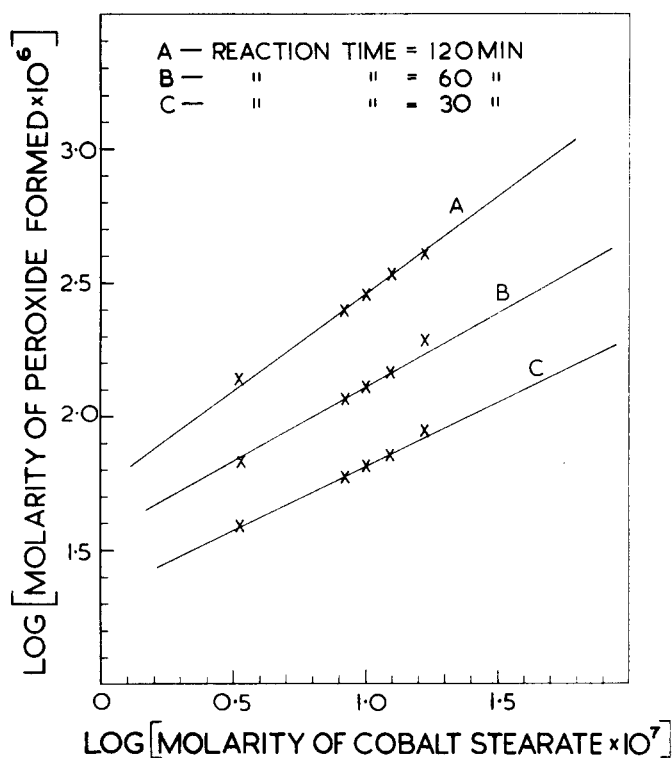
(as illustrated in Figs. 5 and 6). The examination of

FIG. 5. Effect of cobaltous stearate concentration on the rate of the catalyst-hydroperoxide reaction at 37°. (Solvent: cyclohexane. Concentration of linoleic acid = 0.1 M, initially containing 2.5 × 10⁻⁴ M linoleic acid hydroperoxide.)

the temperature dependence of the rate between 25° and 45° in the above-mentioned range of experimental conditions revealed an over-all activation energy of 12.5 kcal (lines *A* and *B* in Fig. 7).

The Cobaltic-Linoleic Acid Reaction. Since the cobaltic catalyst formed in the course of the oxidation did not precipitate from benzene solution but attained a stationary concentration, it was possible to ascertain the kinetic law by variation of catalyst, substrate, and hydroperoxide concentration. It was found that the relationship

$$\frac{d[ROOH]}{dt} \propto [Co^{3+}]^{1/2}[RH]^{3/2}$$

(as illustrated in Figs. 8 and 9) was obeyed when the catalyst concentration was varied between 2 × 10⁻⁵ M and 2 × 10⁻⁴ M, and the substrate concentration between 0.05 M and 0.4 M. The rate was found to be independent of hydroperoxide concentration in the range 10⁻³ to 3.5 × 10⁻³ M (corresponding to a peroxide value range of about 30 to 120, with 0.1 M linoleic acid). Under these conditions the rate of the hydroperoxide-induced oxidation in the absence of metal catalyst was ≤2% of the metal-catalyzed oxidation, and was neglected. The over-all activation energy for the cobaltic-

catalyzed reaction was determined as 14 kcal (lines *C* and *D* in Fig. 7).

DISCUSSION

Apart from the intrinsic interest in connection with the oxidative rancidity of fats, there are several advantages in the use of linoleic acid and its esters in a study of autoxidation: (*a*) Relative ease of obtaining a pure preparation of a 1-4 diene. (*b*) In this structure the weakness of the α-methylenic C...H bond assures the predominant rupture of a single well-defined bond. (*c*) The chain reaction leads, for all practical purposes, in the initial stage to a single oxidation product, the hydroperoxide, which according to Hargrave and Morris (13) corresponds to 98% of the oxygen uptake. This feature does not apply to many other compounds where the multiplicity of products would make a kinetic study more difficult. (*d*) For all practical purposes the hydroperoxide initially formed is conjugated, and therefore the reaction can also be followed conveniently in certain solvents, such as cyclohexane and ethyl alcohol, by direct measurement of light absorption at 230 to 235 mμ, which leads to an increase in accuracy at low concentrations of hydroperoxide.
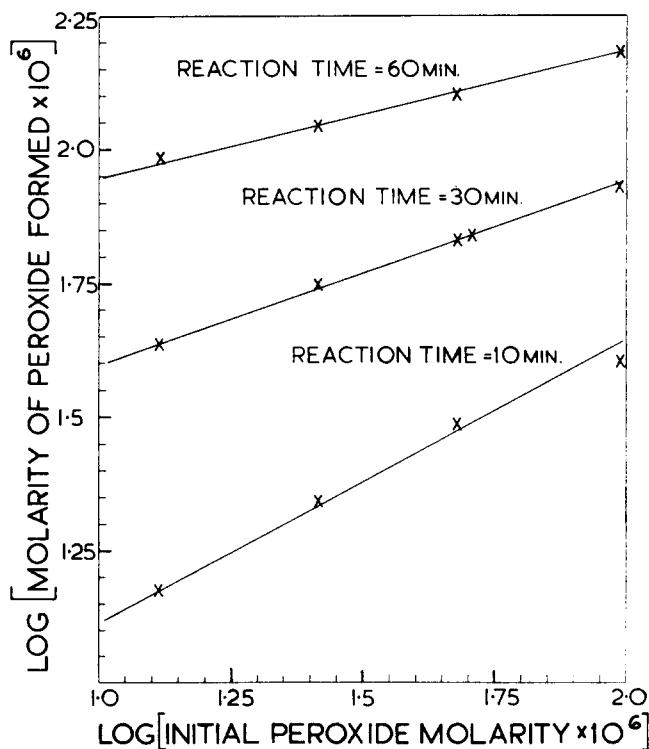

FIG. 6. Effect of linoleic acid hydroperoxide at low concentration on the cobaltous-catalyzed oxidation of linoleic acid at 37°. (Solvent: cyclohexane. Concentrations of linoleic acid and cobaltous stearate 0.1 M and 1.25 × 10⁻⁶ M, respectively.)
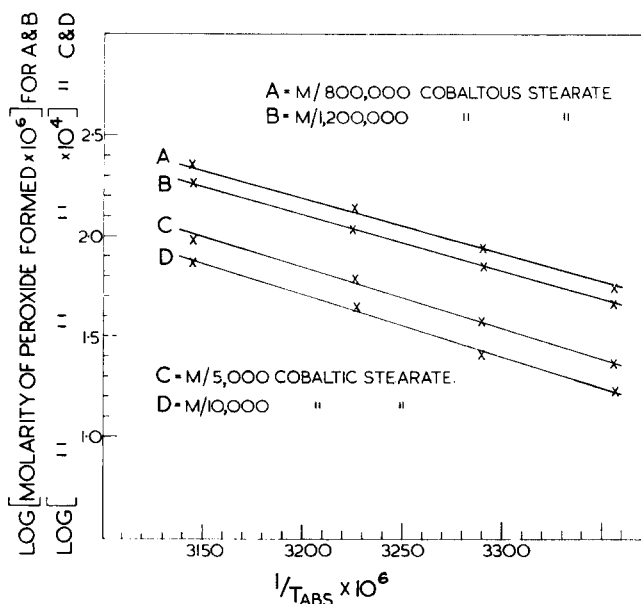
FIG. 7. Evaluation of activation energies for the cobaltous-peroxide (lines *A* and *B*) and cobaltic-linoleic acid (lines *C* and *D*) reactions. (*A* and *B*: linoleic acid concentration = 0.1 M, initially containing 2.5×10^{-4} M linoleic acid hydroperoxide. Solvent: cyclohexane. *C* and *D:* linoleic acid concentration = 0.214 M, initially containing 0.060 M linoleic acid hydroperoxide. Solvent: benzene.)

There are some problems relating to the isomerism of the peroxide which are not yet fully understood. These apply largely to the geometrical isomers of conjugated hydroperoxide formed during oxidation. Our quantitative correlation is in very good agreement with the value of $\epsilon = 28,000$ for the *cis-trans* isomer quoted by Sephton and Sutton (14). The predominant formation of *cis-trans* conjugated hydroperoxide from natu-

rally occurring *cis-cis* linoleic acid would be in agreement with the rules postulated by Nichols *et al.* (15). Recently it was claimed that diperoxides are formed even in the early stages of autoxidation (16). However, it is noteworthy that analysis of the curve obtained by Privett and Nickell supports such diperoxide formation only at peroxide values of ≥ 150. For the purpose of our investigation this was considered an advanced stage, since we were almost exclusively interested in the first 1% of oxidation (corresponding to a peroxide value of ~30). The observed drop in the apparent molar extinction coefficient at a more advanced stage is in close agreement with the data of Privett and Nickell (16).

FIG. 9. Effect of linoleic acid concentration on the rate of its oxidation catalyzed by 10^{-4} M cobaltic stearate in the presence of excess peroxide at 37°. (Solvent: benzene. Initial hydroperoxide content of linoleic acid = 0.1 M.)
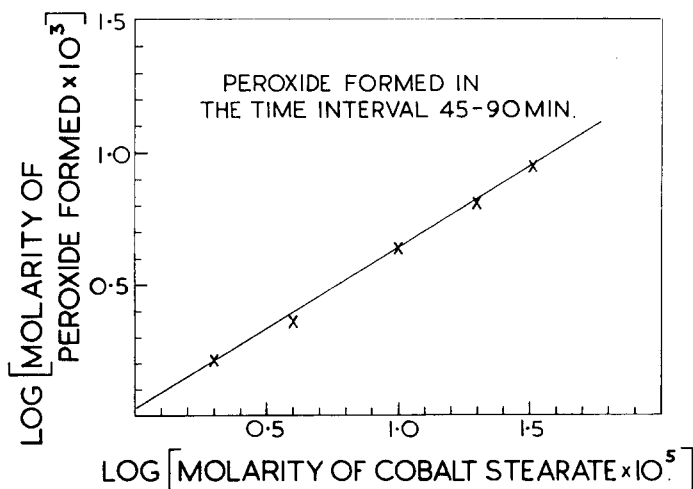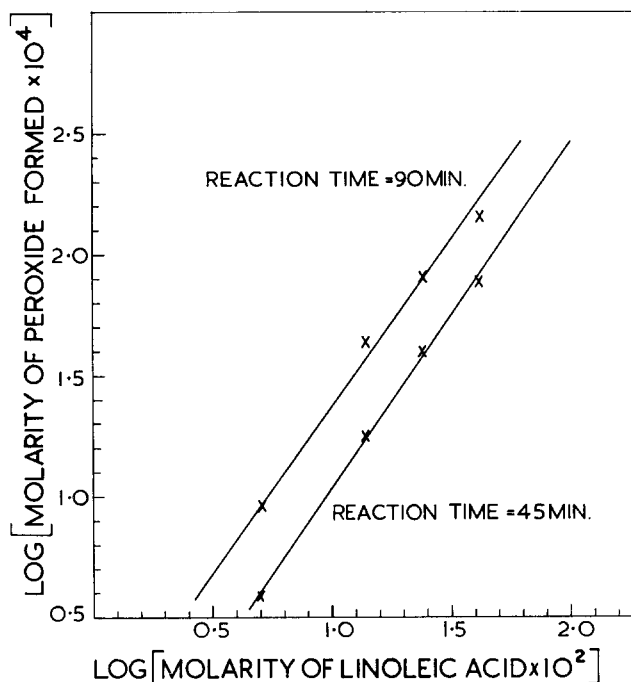

FIG. 8. Effect of cobaltic stearate concentration on the rate of linoleic acid oxidation in benzene in the presence of hydroperoxide at 37°. (Linoleic acid concentration = 0.214 M, initially containing 0.060 M linoleic acid hydroperoxide.)

It is not unexpected that this drop is more marked in the catalyzed than in the uncatalyzed oxidation, since cobaltous stearate would not only be a catalyst for hydroperoxide formation but would also accelerate decomposition of the hydroperoxide and further reactions (e.g., polymerization, diperoxide formation) which are initiated by free radical intermediates of the cobaltous-hydroperoxide reaction. All these reactions lead to loss of conjugation in relation to peroxide content, thus producing the drop in the apparent molar extinction coefficient.

The main emphasis in this investigation was placed on the kinetic aspects of the initiation reaction rather than on the nature of the oxidation products. The initiation process turned out to be of very complex nature. Three distinctly different modes of initiation were ascertained.[1] (a) With the metal in the higher valency state the main reaction was found to be

I(2) $Co^{3+} + RH \rightarrow Co^{2+} + R\cdot + H^{+}$.
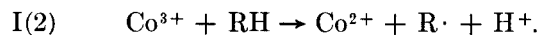
This is well substantiated by the kinetic observations, since $\sqrt{r_i}$ in the general rate equation R(1) is proportional to $[Co^{3+}]^{1/2} [RH]^{1/2}$. The over-all activation energy, ascertained as 14 kcal corresponds to

$$\frac{E_i}{2} + E_p - \frac{E_t}{2}.$$

Assuming an activation energy for propagation of 5 kcal (and neglecting E_t) (cf. reviews by Bateman [1] and Uri [4]) one arrives at a value of 18 kcal for the activation energy of the initiation reaction

$$Co^{3+} + RH \rightarrow Co^{2+} + R\cdot + H^{+}.$$

A calculation based on generally accepted data for k_p and k_t led to an estimate of 10^{10} (mole/liter)$^{-1}$ sec^{-1} for the temperature-independent factor of the rate constant. With such a high activation energy, this reaction is likely to be endothermic in benzene solution, and the assumption that the activation energy corresponds closely to the endothermicity for reactions of this type may be justified. In aqueous solution such a reaction would be very exothermic, if RH = linoleic acid (an estimate of ΔH amounts to -15 kcal). In benzene the cobaltic state (probably in some complex form) is much more stable in relation to the cobaltous state and, if indeed one is justified in using the term oxidation-reduction potential in nonaqueous solvents, the drop of the latter in benzene solution would exceed 1 volt.

It is noteworthy that the reaction

I(3) $Co^{3+} + ROOH \rightarrow Co^{2+} + RO_2^{.} + H^{+}$
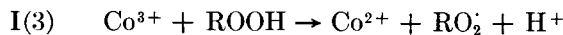
was not found to be significant, which is in contrast to a number of other observations in this field (9). Conceivably, the discrepancy between bond dissociation energy in R...H and in the corresponding hydroperoxide ROO...H is very much larger in the case of linoleic acid than in aldehydes or monounsaturated hydrocarbons. This would explain the predominance of

the cobaltic-substrate reaction in the case of linoleic acid, and presumably also with other 1-4 dienes.

(b) The well-known reduction activation (17) is confirmed by experiments at such low cobaltous concentrations, where, in the absence of peroxide, no significant catalysis is observed. This initiation reaction is represented by

I(4) $Co^{2+} + ROOH \rightarrow Co^{3+} + RO\cdot + OH^{-}$.
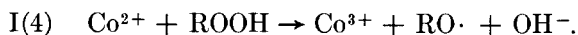
The observed over-all activation energy of 12.5 kcal leads to an estimate of 15 kcal for the activation energy of the above-mentioned reaction. This is a much lower activation energy than that of the corresponding reaction with hydrogen peroxide in aqueous solution, the endothermicity of which would be $\sim$35 kcal, but it is both qualitatively and semiqualitatively consistent with the observations made for the cobaltic-substrate reaction. The cobaltic state appears to be stabilized by comparison with normal aqueous systems to the extent of approximately 1 volt. A calculation of the temperature-independent factor of the rate constant for the cobaltous-peroxide reaction led to a value of 5×10^9 (mole/1)$^{-1}$ sec^{-1}, which is in fair agreement with observations in similar systems.

(c) With the metal in the lower valency state, the experimental evidence also indicates an initiation step which involves the cobaltous ion but no peroxide, and it has been shown that oxygen participates in this step. In an oversimplified manner it may be regarded as an electron transfer reaction of the type

I(5) $Co^{2+} + O_2 \rightarrow Co^{3+} + O_2^{-}$.
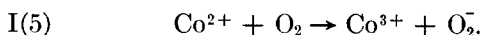
It was pointed out (2) that, in fact, this may be preceded by complex formation between the catalyst, substrate (in solvent), and oxygen according to the scheme:

I(6) $Co^{2+}\cdot O_2(XH) + Co^{2+} \rightarrow Co^{2+} + Co^{3+}X^{-} + HO_2^{.}$.
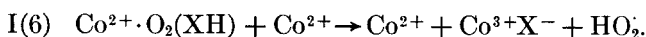
Although it is possible to visualize monomolecular decomposition of the oxygen complex, experimental evidence favors a reaction of a higher order in this region. The anomalous curve in Figure 1, where the order of reaction at first rises with increasing cobaltous concentration, must be due to association of catalyst complexes. Molecular association of heavy metal soaps has been postulated recently (18). Perhaps the initiation reaction in this phase should be represented by:

I(7) $[Co^{2+}(XH)]_n \cdot O_2 \rightarrow [Co^{2+}(XH)]_{n-1} + Co^{3+}X^{-} + HO_2^{.}$.
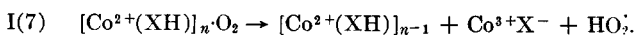
A quantitative interpretation of Figure 1 does not appear possible in view of the complexity of the system, but qualitatively the only possible interpretation would be based on the overlapping of at least three initiation reactions (one of them being negative or inhibitory).

[1] The use of ionic symbols does not necessarily imply the presence of ions as such, in simple form, but is merely an indication of the valency state of the metal. (This is the practice adopted by Bawn and his co-workers.)

It appears that positive initiation is produced mainly by reactions I(7), I(4), and I(2), and inhibition occurs via the reaction:

$$I'(1) \qquad Co^{2+} + RO_2^{\cdot} \rightarrow Co^{3+} + RO_2^{-}$$
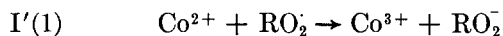
which consumes free radicals. The reproducibility of the observations presented in Figure 3 merits at least a qualitative explanation. The rising curve on the right is explained readily as corresponding closely to cobaltic catalysis. The rising curve on the left is explained by free radical formation of increasing order due to association complexes, which is finally overtaken by an inhibitory reaction of the type I(1) involving a cobaltous association complex and $RO_2^{\cdot}$ radicals. It should be noted that the results in Figure 3 are obtained by sampling at a constant time interval and not at a constant amount of hydroperoxide formation, so that at higher cobalt concentrations the amount of peroxide is such that the cobaltic catalyst is predominant at the time of sampling.

The data in Figure 4 would be difficult, if not impossible, to explain unless the assumption is upheld that an oxygen complex, the formation of which is endothermic (to the extent of $\sim$15 kcal), participates in the initiation reaction. This is important in the whole understanding of autoxidation, since it lends support to the hypothesis that the initial formation of hydroperoxide is due to the interaction between trace-metal impurities and molecular oxygen (3, 4). Once small quantities of peroxide have been formed the trace-metal reduction activation becomes important, and finally the higher valency state becomes effective as catalyst. The tracer experiments proved that a cobaltic linoleate compound was formed during the catalysis.

It would, in general, be an oversimplification to ascribe catalytic activity in autoxidation to one particular valency state, because it appears that a cyclic process which involves both the higher and the lower valency state occurs. This results in a certain stationary concentration of free radicals on which the propagation of the chain reaction depends. Among the heavy metal stearates, it was the cobaltous-cobaltic system which was found unequaled in its catalytic efficiency, but one must not generalize: e.g., among the porphine derivatives the ferrous-ferric system is the most active. Certain factors which influence the lability with regard to electron transfer or hydrogen transfer, and are not yet completely understood, appear to play a very important role in determining the catalytic efficiency of heavy metal catalysts which depends not only on the nature of the metal but also on its environment.

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