The Effect of Copper, Manganese and Cobalt Acetates on the Autoxidation of *trans*-9,*trans*-11-Octadecadienoic Acid in 90% v/v Aqueous Acetic Acid

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ABSTRACT

The autoxidation of *trans*-9,*trans*-11-octadecadienoic acid in 90% v/v aqueous acetic acid has been studied, at 80 C, with and without copper, manganese and cobalt acetate. The initial 9,11-octadecadienoic acid concentration was 0.05 M in most of the experiments. The metallic acetate concentrations were 10^{-5} to 10^{-2} M. Copper and manganese acetates retard the autoxidation. With copper acetate, this retardation involves both the induction period and the rapid autocatalytic stage. Manganese acetate prolongs the induction period. A slightly lowered rate is observed at low cobalt acetate concentrations ($\sim 10^{-5}$ M), but higher cobalt acetate concentrations clearly accelerate the autoxidation.

INTRODUCTION

The mechanism of autoxidation of conjugated polyunsaturated compounds is different from that of nonconjugated ones (1). Thus salts of heavy metals such as copper, manganese and often cobalt retard the autoxidation of organic aliphatic acids containing conjugated double bonds, such as sorbic acid in water (2) and in acetic acid (3). High concentrations ($\geqslant 10^{-2}$ M) of cobalt salts retard the autoxidation of sorbic acid in water, but low concentrations (10^{-5} to 10^{-3} M) either have no effect or slightly accelerate the reaction. In acetic acid, cobalt salts clearly retard the reaction, but this retardation is weaker than with manganese and copper salts. Copper and manganese acetates retard the autoxidation of β-eleostearic acid (4,5) and α-eleostearic acid (6) in acetic acid, but cobalt acetate only at low concentrations ($< 10^{-4}$ M). At high concentrations ($> 10^{-4}$ M), cobalt acetate accelerates these reactions. Also the effects of heavy metal acetates on the autoxidation of β-eleostearic acid in 0.025 molar concentration in a 90% acetic acid-water mixture at 40 C were investigated recently (L. Pekkarinen, unpublished data). Copper and manganese acetates clearly retarded the reaction, whereas cobalt acetate at concentrations varying from 10^{-5} to 10^{-2} M had very little effect on the rate. *trans*-9,*trans*-11-Octadecadienoic acid with only two conjugated double bonds was studied with copper, manganese and cobalt acetates to see how this diene differs from β-eleostearic acid, since β-eleostearic acid (*trans*-9,*trans*-11,*trans*-13-octadecatrienoic acid) contains three conjugated double bonds. A 90% v/v acetic acid-water was chosen as the solvent, because the reaction proceeds in it at convenient rates, but is too slow in pure acetic acid to permit accurate measurements.

EXPERIMENTAL PROCEDURES

The reactions were conducted in a jacketed round-bottomed flask at 80±0.1 C maintained by water circulated from a constant temperature water bath. Oxygen could be passed through the reaction mixture and the oxygen pressure within the reaction flask could be adjusted with a water manometer. An oxygen pressure corresponding to 70 cm water over 1 atm was employed in the experiments. The reaction flask contained a magnetic rod for mixing the contents and 50 ml of the 90% v/v acetic acid-water mixture or its solution of a metallic acetate was added to the reaction flask. The solution was warmed for 15 min. A weight of *trans*-9,*trans*-11-octadecadienoic acid sufficient to give a concentration of 0.05 or 0.1 M was added to the reaction vessel. When the acid had dissolved, a 5 ml sample was taken; oxygen was then passed into the space above the reacting mixture and the pressure was adjusted to the preselected level. This was taken to be zero time. The 5 ml sample was discharged into and diluted with 94% ethanol. Sulphuric acid was added so that its final dilution was 0.01 N. The absorbance of the resulting solution was measured at 231 nm. A correction was made for acetic acid. The 5 ml samples of the reaction mixture were taken at appropriate intervals during the reaction and their absorbance measured. The extent of the reaction in per cent was calculated on the basis of the absorbance readings.

trans-9,*trans*-11-Octadecadienoic acid was prepared from ricinelaidic acid, which in turn was synthesized from ricinoleic acid (technical, ca. 90%, Schuchardt AG) by the method of Kass and Radlove (7). The ricinelaidic acid melted at 48-50 C after it had first crystallized from ether and then from a 1:3 ether-petroleum ether mixture at -25 C. Ricinelaidic acid was converted to *trans*-9,*trans*-11-octadecadienoic acid by the estolide method of Schneider et al. (8). The product was recrystallized twice from ethanol at -15 C. The absorptivity of the acid in methanol at 231 nm was 106 (molar absorptivity $2.97 \cdot 10^4$). According to the absorptivity reported by Schneider et al. (8), the acid was ca. 86% pure. The acid was stored at -25 C and samples of the same batch of crystals were used in all the experiments.

Acetic acid (99-100%) and copper acetate dihydrate were guaranteed reagents from E. Merck AG; manganese acetate tetrahydrate, a laboratory reagent from Riedel-de Haen AG; and cobalt acetate tetrahydrate, a laboratory reagent from British Drug Houses Ltd.

RESULTS AND DISCUSSION

The results of the experiments are plotted in Figures 1, 2 and 3. The rate of autoxidation of *trans*-9,*trans*-11-octadecadienoic acid in the absence of a metal acetate increases with the initial acid concentration, as with previously studied conjugated acids (3-6); but the rate is low compared to the rate of oxidation of β-eleostearic acid. No reaction was found to have occurred during 6 hr when manganese acetate was present in 10^{-3} M and 10^{-2} M concentrations, and reproducible results were not obtained when copper acetate was present in the same concentrations. The curves in the figures show that both copper and manganese retard the reaction by prolonging the induction period. In addition, copper clearly slows the rapid stage of the reaction. Manganese acetate at 10^{-2} M concentration does not shorten the induction period, as it does the induction period in the autoxidation of α- and β-eleostearic acids in acetic acid (5,6). Manganese acetate in the same concentration does not shorten the induction period in the autoxidation of β-eleostearic acid when the solvent is 90% v/v aqueous acetic acid. Cobalt acetate seems to retard the autoxidation of *trans*-9,*trans*-11-octadecadienoic acid slightly when its concentration is 10^{-5} M, but accelerates

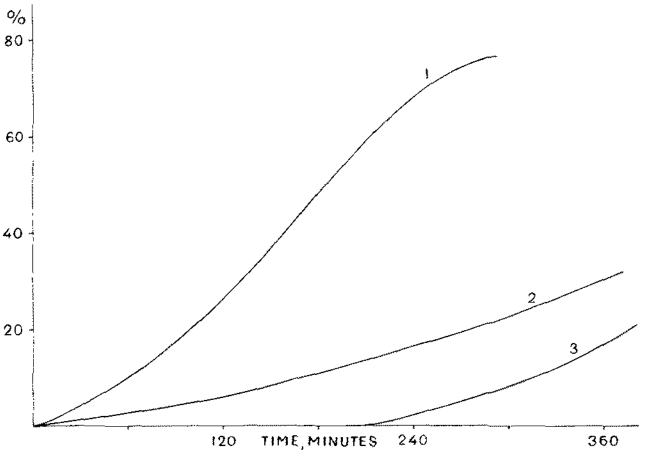

FIG. 1. The effect of copper acetate on the progress of the oxidation of *trans*-9,*trans*-11-octadecadienoic acid (0.05 M) in 90% acetic acid-water at 80 C. 1: No added metal acetate; 2: 10^{-5} M in copper acetate; 3: 10^{-4} M in copper acetate.

the reaction when its concentration is 10^{-3} or 10^{-2} M. This effect is the same as with α- and β-eleostearic acids in acetic acid (5,6). Cobalt acetate in concentrations from 10^{-5} to 10^{-2} M does not affect the rate of autoxidation of β-eleostearic acid in 90% v/v acetic acid (L. Pekkarinen, unpublished data). In general, salts of heavy metals accelerate the autoxidation, as does also cobalt acetate in the present study at higher concentrations. The acceleration of the reaction is probably due to the decomposition of the peroxidic compounds by metal salts.

The results of this study confirm the results of earlier investigations of the autoxidation of acids containing conjugated double bonds. The retardation of the autoxidation reaction by copper and manganese acetates is evident also according to these results. This retardation probably results because the accelerating effect is small owing to the low concentration of the peroxy compounds and the metal acetates evidently function as effective antioxidants. This effect may result from the addition of molecular oxygen either directly or by a way of peroxy radical to the conjugated double bond system (1), and the resulting peroxy diradical is decomposed by paramagnetic metal ion. The process is evidently similar to the quenching of triplet states by paramagnetic ions (9). As no permanent change occurs in the valency state of metal ion in this type of process, the antioxidant effects of both reducible (Cu^{++}) and oxidizable (Mn^{++}, Co^{++}) ions are understandable. This antioxidant effect may also thus become evident both as a prolongation of the induction period and a retardation of the rapid (autocatalytic) stage of the autoxidation.

Salts of heavy metals have also been found to retard certain autoxidation reactions where monoradicals are formed as intermediates. A change in the valency state of metal ion has probably started to occur (10,11).

$$RO_2^{\bullet} + M^{2+} \rightarrow RO_2^{-} + M^{3+}$$

$$R^{\bullet} + M^{2+} \rightarrow \text{inactive products} + M^{+}$$

Other factors have also been claimed to be responsible for the retarding effect observed with metal salts (12).

The following stages may be assumed to occur if a diradical is formed as an intermediate (4) (A is an acid containing conjugated double bonds):

$$A + O_2 \xrightarrow{k_1} AO_2^{\bullet\bullet} \quad [1]$$

$$A + AO_2^{\bullet\bullet} \xrightarrow{k_2} AO_2A \quad [2]$$

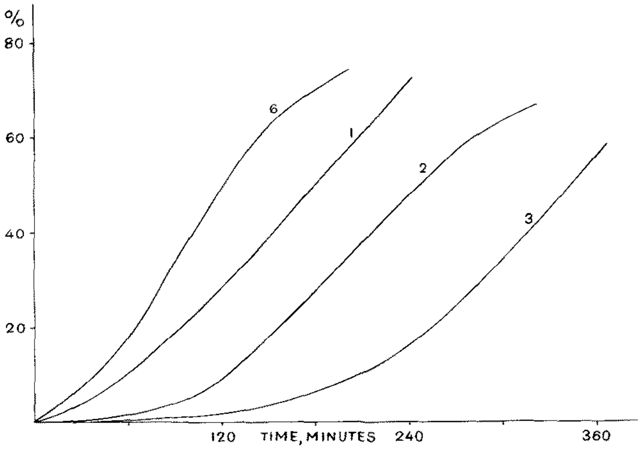

FIG. 2. The effect of manganese acetate on the progress of the oxidation of *trans*-9,*trans*-11-octadecadienoic acid in 90% acetic acid-water at 80 C. 1: Acid concentration 0.05 M and no added metal acetate; 2: acid concentration 0.05 M and manganese acetate concentration 10^{-5} M; 3: acid concentration 0.05 M and manganese acetate concentration 10^{-4} M; 6: acid concentration 0.1 M and no metal acetate added.

$$AO_2A \xrightarrow{k_3} \text{radicals} \xrightarrow[\text{rapid}]{\text{oxygen}} 2\,AO_2^{\bullet\bullet} \quad [3]$$

$$AO_2^{\bullet\bullet} + M^{++} \rightleftharpoons [\text{complex}] \xrightarrow{k_4} AO_2 + M^{++} \quad [4]$$

$$AO_2^{\bullet\bullet} + AO_2^{\bullet\bullet} \xrightarrow{k_5} \text{inactive products} \quad [5]$$

The rate-determining stage is evidently reaction 2. If we assume that reaction 1 is no longer significant in the advanced stage of reaction and that the concentrations of $AO_2^{\bullet\bullet}$ and AO_2A remain constant, the rate equation will be:

$$-\frac{d[A]}{dt} = k_2[A]\,[AO_2^{\bullet\bullet}] = \frac{k_2[A]}{k_5}\left\{ k_2[A] - k_4 \right\}$$

Taking into account that the rate constant k_4 includes the metal ion concentration, we can write $k_4 = k_4'[M^{++}]$. Then

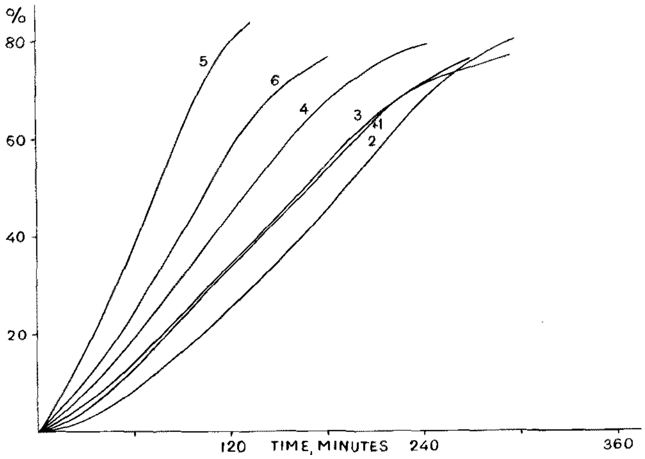

FIG. 3. The effect of cobalt acetate on the progress of the oxidation of *trans*-9,*trans*-11-octadecadienoic acid in 90% acetic acid-water at 80 C. 1: Acid concentration 0.05 M and no added metal acetate; 2: acid concentration 0.05 M and cobalt acetate concentration 10^{-5} M; 3: acid concentration 0.05 M and cobalt acetate concentration 10^{-4} M; 4: acid concentration 0.05 M and cobalt acetate concentration 10^{-3} M; 5: acid concentration 0.05 M and cobalt acetate concentration 10^{-2} M; 6: acid concentration 0.1 M and no added metal acetate.

the rate equation takes the following form:

$$-\frac{d[A]}{dt} = \frac{k_2[A]}{k_5}\left\{k_2[A] - k_4'[M^{++}]\right\}$$

This equation clearly shows that a metal salt may lower the rate of autoxidation. The equation obtained is similar to what Ingold has presented for the retardation of the limiting rate by metal salts when monoradicals are intermediates in the autoxidation (10).

Peroxides may be formed in the autoxidation reactions and these may decompose to radicals under suitable conditions. It seems that cobalt is effective in this way, but not copper or manganese; k_4' may be small with cobalt but larger with manganese and especially copper. Thus it is understandable that cobalt may accelerate, but manganese and copper decelerate the autoxidation reaction.

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[Received December 21, 1971]