The Influence of Metal Acetates on the Oxidation of Sorbic Acid by Molecular Oxygen in Acetic Acid and Comparison of the Results with Those for Eleostearic Acids

LAURI PEKKARINEN

Central Laboratory of OTK, Helsinki 50, Finland

The oxidation of sorbic acid (initial concentration 0.07 M) by molecular oxygen in acetic acid containing heavy metal acetates was studied at 80°C. The oxidation is strongly inhibited by copper(II) acetate in 10^{-5} molar concentration, by manganese acetate in 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} molar concentrations, and by cobalt acetate in 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} molar concentrations. The inhibition by cobalt acetate is less pronounced than that by manganese acetate and, especially, copper acetate. An increase in the initial sorbic acid concentration leads to an acceleration of the autoxidation. The results are compared with those previously reported for α-eleostearic acid and β-eleostearic acid. The reaction mechanism is discussed in terms of the influence of the metal salts.

In a series of investigations dealing with the oxidation of compounds with conjugated double bonds by molecular oxygen in the presence of salts of heavy metals, the oxidation of sorbic acid in water[1] and that of β- and α-eleostearic acids in acetic acid[2-4] have been studied. Also the effect of metal salts in 90 % acetic acid — water mixture on the oxidation of β-eleostearic acid[5] and *trans,trans*-9,11-octadecadienoic acid[6] have been investigated. Copper salts were found to retard the reactions. Manganese salts retarded the reactions at concentrations exceeding 10^{-5} M. At a manganese concentration of 10^{-2} M there is no induction period in the reactions of α- and β-eleostearic acids in acetic acid although the rapid stages of the reactions are clearly decelerated. The influence of cobalt varied slightly with the experimental conditions. High cobalt concentrations ($\geq 10^{-2}$ M) retarded slightly the autoxidation of sorbic acid in water, but accelerated the oxidation of α- and β-eleostearic acids in acetic acid. In order to be able to compare the autoxidation of sorbic acid and eleostearic acids, we have now investigated the oxidation of sorbic acid in acetic acid both with and without metal acetates present. Work on the retardation of the autoxidation reactions by metal salts has been reviewed in an earlier publication.[2]

EXPERIMENTAL

Chemicals. Sorbic acid was a *purum* product from Fluka that was purified by re-crystallization from water. Copper acetate monohydrate and 99 – 100 % acetic acid were guaranteed reagents from E. Merck, cobalt acetate tetrahydrate was a laboratory reagent from British Drug Houses, and manganese acetate tetrahydrate an analytical reagent from Riedel-de Haën.

Performance of the experiments. The reactions in acetic acid were conducted as described earlier.[2] They were followed by taking samples of the reaction mixtures at intervals and diluting them with water before measuring their absorbance at 262 nm. The solutions were 0.01 N in sulphuric acid. The degrees of advancement of the reactions were calculated from measured absorbances after these had been corrected for evaporated acetic acid.
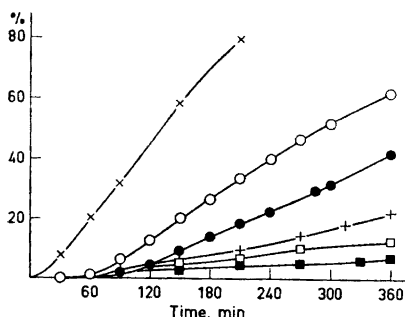
RESULTS AND DISCUSSION

Fig. 1. The effect of cobalt acetate on the progress of oxidation of sorbic acid (0.07 M) in acetic acid at 80°C. O, no added metal salt; ●, 10^{-5} M; +, 10^{-4} M; □, 10^{-3} M; ■, 10^{-2} M cobalt acetate. Symbols × show the course of reaction when the initial concentration of sorbic acid is 0.14 M and no metal salt is present.
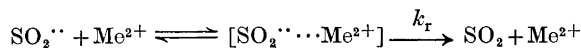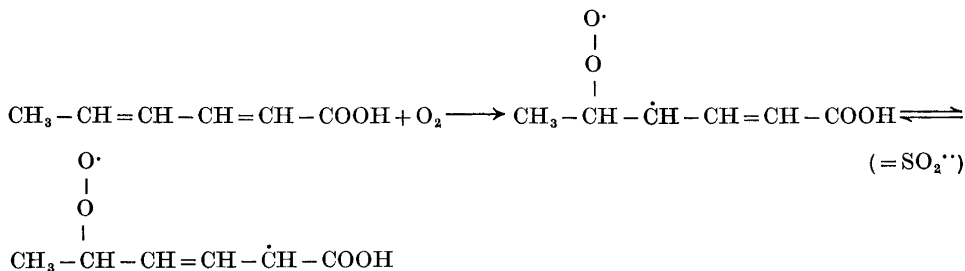
The curves in Fig. 1 show the accelerating effect of increasing initial concentration (0.07 and 0.14 M) of sorbic acid on its oxidation in acetic acid at 80°C and the retardation by cobalt acetate of the reaction of sorbic acid (0.07 M) in the same solvent at the same temperature. When the initial concentrations of sorbic acid and copper acetate in acetic acid were 0.07 M and 10^{-5} M, respectively, no reaction was detected over a period of 360 min. The degree of advancement of the reaction of sorbic acid (initial concentration 0.07 M) in the presence of 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} mol/l of manganese acetate during 360 min was at most 6 %. Taking into account that a correction was necessary owing to the evaporation of acetic acid from the reaction vessel, it cannot be decided with certainty whether the reaction advanced at all in the presence of manganese; at least the reaction progressed very little.

On the basis of the results presented above and those reported earlier, the following conclusions can be drawn about the oxidation reactions of sorbic and α- and β-eleostearic acids in acetic acid in the presence and absence of heavy metal acetates:

1. The rates of oxidation of sorbic acid and the eleostearic acids vary with the initial concentration of the acid in such a manner that the relative rate increases with concentration. The rate of autoxidation of sorbic acid is clearly lower than the rates of autoxidation of α- and β-eleostearic acids, which latter are higher already at 50°C than the rate of oxidation of sorbic acid at 80°C. No autoxidation of sorbic acid was observed during 6 h at 50°C when the initial concentration of sorbic acid was 0.01, 0.03, or 0.07 M.

2. Copper and manganese acetates retard the autoxidation reactions of sorbic and both eleostearic acids. Cobalt acetate in all the employed concentrations retards the autoxidation of sorbic acid. Low concentrations of cobalt acetate retard the autoxidation of α- and β-eleostearic acids, but high concentrations ($> 10^{-4}$ M) accelerate the reactions. Manganese acetate in 10^{-2} M concentration did not shorten the induction period in the reaction of sorbic acid as it does in the case of α- and β-eleostearic acids.

The retardation of autoxidation reactions of compounds with conjugated double bonds by heavy metal salts has been previously attributed to the formation of labile complexes by the metal ions with diradical peroxy-compounds.[2,7] The binding of metal ions to other possible radicals can hardly be expected to occur at the oxygen pressure (1 atm) employed in our experiments. The metal ion may be regenerated when these complexes decompose. This regeneration is necessary since the formation of a highly stable complex would lead only to a prolongation of the induction period. The obtained results show, however, that the metal salt influences also the rapid stage of the autoxidation by retarding it. The formation of a labile complex by a peroxy radical and a divalent metal ion may be represented as follows (sorbic acid = S):

$$CH_3-CH=CH-CH=CH-COOH+O_2 \longrightarrow \underset{\substack{| \\ O \\ | \\ O \cdot}}{CH_3-CH-\dot{C}H-CH=CH-COOH} \rightleftharpoons$$

$$(=SO_2^{..})$$

$$\underset{\substack{O \cdot \\ | \\ O \\ |}}{CH_3-CH-CH=CH-\dot{C}H-COOH}$$

$$SO_2^{..} + Me^{2+} \rightleftharpoons [SO_2^{..}\cdots Me^{2+}] \xrightarrow{k_r} SO_2 + Me^{2+}$$

The spins of the unpaired electrons in the $SO_2^{..}$-radical may be parallel and the spin moment may hence differ from zero. The $SO_2^{..}$-radical will then be paramagnetic. The metal ions that we have studied are also paramagnetic and consequently the decomposition of the $SO_2^{..}$-radicals by the action of the metal ions is comparable with the quenching of triplet states by heavy metal salts.[8,9]

If the rate of the rate-determining stage of the autoxidation reactions under study can be expressed by

$$\frac{d[S]}{dt} = k_p[S][SO_2^{..}]$$

the concentration of $SO_2^{..}$ and hence the rate is lower in the presence of a metal ion than in its absence. A rate equation expressing this influence of metal ions has been presented earlier.[2] In some cases the metal-radical

complex may decompose slowly (k_r small) and the metal ion may primarily prolong the induction period. This seems to be the case when eleostearic acids are oxidized in the presence of low concentrations of manganese acetate.[3,4]

The markedly shorter induction period noted in the reactions of α-eleostearic acid and, especially, β-eleostearic acid in the presence of manganese acetate in 10^{-2} M concentration does not seem to occur with sorbic acid, although, as mentioned, this is somewhat uncertain. The shortening of the induction period in the reactions of β-eleostearic acid have been discussed earlier.[3] One possibility then considered was that the acceleration of the initial stage at high manganese concentrations is due to activation of oxygen, although the mechanism remains unaltered. One further alternative is that the species oxidized at high manganese concentrations is manganese eleostearate, which may react directly with oxygen, whereupon the contribution of the chain reaction would be smaller. The formation of such a salt may be less extensive in the case of sorbic acid or the salt may not be oxidized. The available experimental data do not permit a more detailed clarification of the shortening of the induction period in the autoxidation of eleostearic acids in the presence of high manganese concentrations. It may be mentioned, that this type of shortening of the induction period has not been observed in 90 % acetic acid by β-eleostearic acid [5] and trans,trans-9,11-octadecadienoic acid.[6]

Heavy metal salts sometimes accelerate the autoxidation of conjugated compounds. This acceleration can be attributed to the decomposition of peroxidic compounds formed in the oxidation by the metal salts. The rate of decomposition of peroxidic compounds is depending on their nature and on the metal ion in question. We have found earlier that the concentrations of such peroxidic compounds are very low in the oxidation of sorbic acid and as a result the acceleration of the oxidation resulting from their decomposition by metal ion is slight. However, the concentration of such peroxidic compounds is higher in solutions of eleostearic acid in acetic acid and accordingly an acceleration is observed at high cobalt concentration in acetic acid. The effect of copper and manganese on the decomposition of peroxidic compounds may be small. The accelerating effect of a metal may be of a different order in the metal concentration than its retarding effect. In addition, the accelerating effect may rise to a maximum at a relatively low metal concentration owing to the high rate of peroxidic decomposition, i.e. even a low metal concentration is sufficient to decompose all the peroxides as they are formed. The acceleration may, however, be small if the peroxide concentration remains low. This may be the case in the oxidation of sorbic acid in water containing a cobalt or ferric salt in low concentrations, where a slight acceleration was noted.[1] On the basis of the observed effect of cobalt acetate on the oxidation of eleostearic acids in acetic acid,[3,4] it seems that the retardation reaction is of a lower order in the metal concentration than the acceleration reaction.

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