Thermal Behaviour of Ferric Laurate

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Thermal behaviour of ferric laurate has been studied by means of a derivatograph. There is a phase transition in the temperature region of 55-105° before the salt starts to decompose around 300°. The decomposition is a multistep process which can be explained by a free radical mechanism similar to that proposed for calcium salt of monocarboxylic fatty acids. Various thermal parameters have also been evaluated.

DERIVATOGRAPHIC analysis has been widely used in the study of thermal behaviour of various metallic salts and complexes. Recently Ray Chaudhuri et al.¹ reported thermal studies of calcium propionate monohydrate and evaluated various thermal parameters. In the present paper we have investigated the thermal behaviour of ferric laurate, a metallic soap. The latter has been used as initiator in the polymerization of various monomers²-⁶.

Materials and Methods

Ferric laurate was prepared by the usual procedure involving double decomposition of sodium laurate and ferric chloride solution. To ferric chloride solution in water was added sodium laurate (prepared from sodium ethoxide and lauric acid) in 1:1 ethanol-water mixture dropwise with constant stirring. The precipitated ferric laurate obtained was filtered and washed repeatedly with water followed by ethanol. For further purification it was dissolved in benzene, filtered and dried in a lyophyllizer. Elemental analysis confirmed the compound to be iron trilaurate.

A Paulik-Paulik-Erdey type MOM derivatograph was used for thermal analysis. Sample of ferric laurate (100 mg) was heated in a platinum crucible at a heating rate of about 10° min⁻¹ in air. Experiments carried out at a slow rate of heating at 3° min⁻¹ in an inert atmosphere of argon did not show any improved resolution.

Infrared spectra were measured in chloroform solution on a Beckman Acculab T.M. 4 infrared spectrophotometer.

Results and Discussion

The derivatogram of ferric laurate is shown in Fig. 1. It is found from the TG curve that ferric laurate is fairly stable up to 150° after which it starts to decompose. This decomposition is not associated with any oxidation in the presence of air, since essentially similar thermograms were obtained when the thermal analysis was done under an inert atmosphere of argon.

It can be seen from Fig. 1 that in the temperature region of 55-105° there is a well-resolved small endotherm in the DTA curve. This is found even after repeated thermal analysis. This endotherm may indicate some sort of phase transition. Similar type of phase transition, although exothermic in nature, has also been observed in the case of thermal analysis of calcium propionate¹. This phase transition is found to be reversible by the following experiment. A sample of ferric laurate was heated at 110° for 1 hr to allow for complete phase transition and then cooled in a desiccator. This sample was then again analysed in the derivatograph and the same type of transition was observed again, indicating the reversibility of the phase transition. Infrared spectra of the salt before and after the phase transition also showed no difference. From the foregoing it may be considered that this endothermic phase transition without weight loss is due to the melting of the salt in this temperature region.

The decomposition of ferric laurate occurs after phase transition. The first step of decomposition takes place when the temperature rises to about 300°. The weight loss associated with the first step is 31.9% as can be seen from the TG curve. The decomposition is also accompanied by the evolution of gas, an aqueous solution of which is acidic. The acidity may be due to the carbonic acid which might have been formed by the evolved carbondioxide in the presence of water. The thermal decomposition in the first step may thus be represented as follows:

\[
\text{heat} \quad [\text{CH}_3(\text{CH}_2)_{10}\text{COO}]_2\text{Fe} \rightarrow [\text{CH}_3(\text{CH}_2)_{10}\text{COO}]_2\text{Fe} + \text{CH}_3(\text{CH}_2)_{10} + \text{CO}_2
\]

The activation energy for the first step of decomposition has been calculated by the three widely used kinetic equations, namely Horowitz and Metzger's equation⁷, Freeman and Carroll's equation⁸ and modified Coats and Redfern's equation⁹ and found to be \(8.43 \times 10^3\), \(7.31 \times 10^3\) and \(6.59 \times 10^3\) J mole⁻¹ respectively. The order of reaction, as calculated from the analysis of TG curves using Freeman and Carroll's equation, i.e. from the plot
in this step corresponding to that expected for the formation of FeCO₃. This multistep decomposition of ferrous laurate may be explained by a free radical mechanism similar to that suggested by Hites and Biemann¹⁰ for the pyrolysis of calcium salt of monocarboxylic fatty acids:

$$[\text{CH}_3(\text{CH}_2)_{10}\text{COO}]_2\text{Fe}$$

$$\downarrow$$

$$\begin{align*}
\text{CH}_3(\text{CH}_2)_{10}^+ + \text{CH}_3(\text{CH}_2)_{10} + \text{FeCO}_3 \\
\text{CH}_3(\text{CH}_2)_{10}^+ + \text{CH}_3(\text{CH}_2)_{10} \rightarrow \text{CH}_3(\text{CH}_2)_{10}^C(\text{CH}_2)_{10}^C(\text{CH}_2)_{10}^C
\end{align*}$$

Moreover, the CH₃(CH₂)_{10} radical may also disproportionate to other alkyl radicals causing thereby the multiple steps as observed in the DTA curve.

The enthalpy changes for the decomposition processes as calculated by the method of Tsuchiya et al.¹¹ using copper sulphate pentahydrate as a standard, are quite high. The value obtained for the first step of decomposition of ferric laurate to ferrous laurate is $-2.12 \times 10^4$ J mole⁻¹ and that for the decomposition of ferrous laurate to FeCO₃ is $-8.59 \times 10^4$ J mole⁻¹. The enthalpy change for the phase transition step is $+61 \times 10^2$ J mole⁻¹.

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**References**