THERMOGRAVIMETRY OF DIHYDROXYVIOLANTHRONE ESTERS *

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ABSTRACT

Dihydroxyviolanthrone esters of straight chain alkanoic acids contain a thermally stable aromatic system connected by an ester linkage to an aliphatic hydrocarbon moiety. These esters provide excellent models for studying the different pyrolysis behavior of aliphatic and aromatic structures. Using dynamic and isothermal thermogravimetry, the effect of atmosphere on volatilization, the variation of stability with chain length of the alkanoic acid, and the volatilization kinetics have been studied.

INTRODUCTION

Pyrolysis of high molecular weight aliphatic compounds such as polyolefins effects complete volatilization to a complex mixture of low molecular weight fragments. On the other hand, many high molecular weight aromatic compounds pyrolyze with the formation of a carbonaceous residue and only a small volatile fraction of low molecular weight. The possibility of studying both forms of pyrolysis within a single system is afforded by straight chain esters (I) of dihydroxyviolanthrone, which join, through an ester linkage, a very stable aromatic nucleus with an aliphatic hydrocarbon moiety.
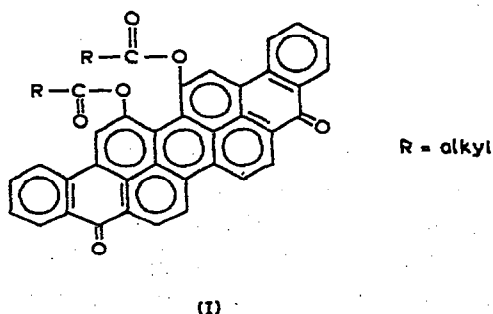
(I)

EXPERIMENTAL DETAILS

Materials

Dihydroxyviolanthrone and all dihydroxyviolanthrone esters were American Cyanamid Company research samples [1].

Procedure

Thermogravimetric instrumentation manufactured by the Perkin-Elmer Corporation, TGS-2, was used in this study. The temperature scale of the instrument was calibrated with Curie point standards, according to the manufacturer's specifications. A dynamic gas atmosphere was maintained by a 25 mL min^{-1} stream of either dry air or dry nitrogen. In the case of simultaneous dynamic thermogravimetry/derivative thermogravimetry (TG/DTG) scans, the heating rate was 10°C min^{-1}. In the isothermal experiments, the furnace was heated to the desired temperature before admission of the weighed sample. The recorder drive was started simultaneously.

RESULTS AND DISCUSSION

The thermal curves of free dihydroxyviolanthrone in air and nitrogen atmospheres are shown in Fig. 1. It is seen that in air the compound is stable up to about 480°C and then volatilizes almost completely, with the maximum volatilization rate, given by the maximum of the DTG curve, at 497°C. In the non-reactive nitrogen atmosphere, the compound is very stable, with a small, gradual weight loss beginning above 425°C. This suggests that the volatilization of this stable aromatic substance is only made possible by thermo-oxidation. Volatilization under purely pyrolytic conditions does not occur.

Figure 2 shows the thermal curves in air and nitrogen for dihydroxyviolanthrone stearate. In air, two major weight losses are observed: the lower temperature loss occurs in two steps, resulting in a double peak for the DTG trace, with rate maxima at 289°C and 311°C; the higher temperature weight loss occurs at 567°C. In the non-reactive nitrogen atmosphere, only the lower temperature weight loss is observed, with a rate maximum at 311°C and a shoulder at 298°C. No distinct higher temperature process is encountered. Hence, while the lower temperature reaction is purely pyrolytic, the higher temperature decomposition must be a thermo-oxidation.

The thermal curves of dihydroxyviolanthrone esters of other straight chain alkanoic acids are shown in Fig. 3. In an air atmosphere, one observes in each case a pyrolytic low temperature decomposition followed by a higher temperature thermo-oxidation. Table 1 summarizes the DTG peak temperatures of the two decomposition processes for the different esters.

In Fig. 4, the DTG peak temperatures for the two reactions are plotted against the number of carbon atoms contained in the ester chain. The C_7 ester shows maximum
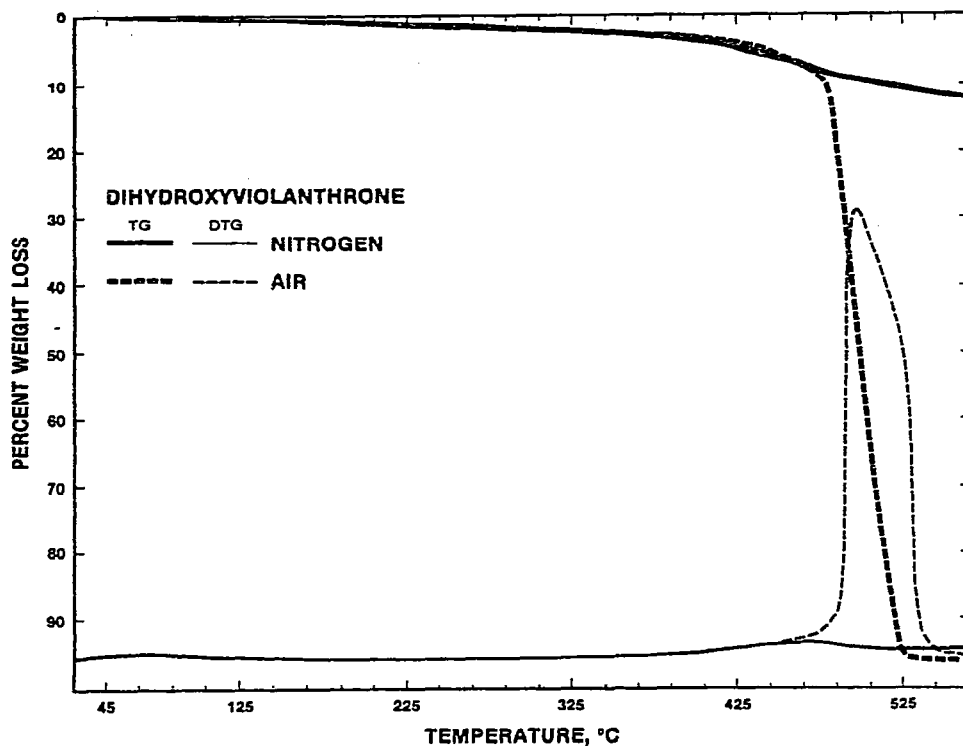
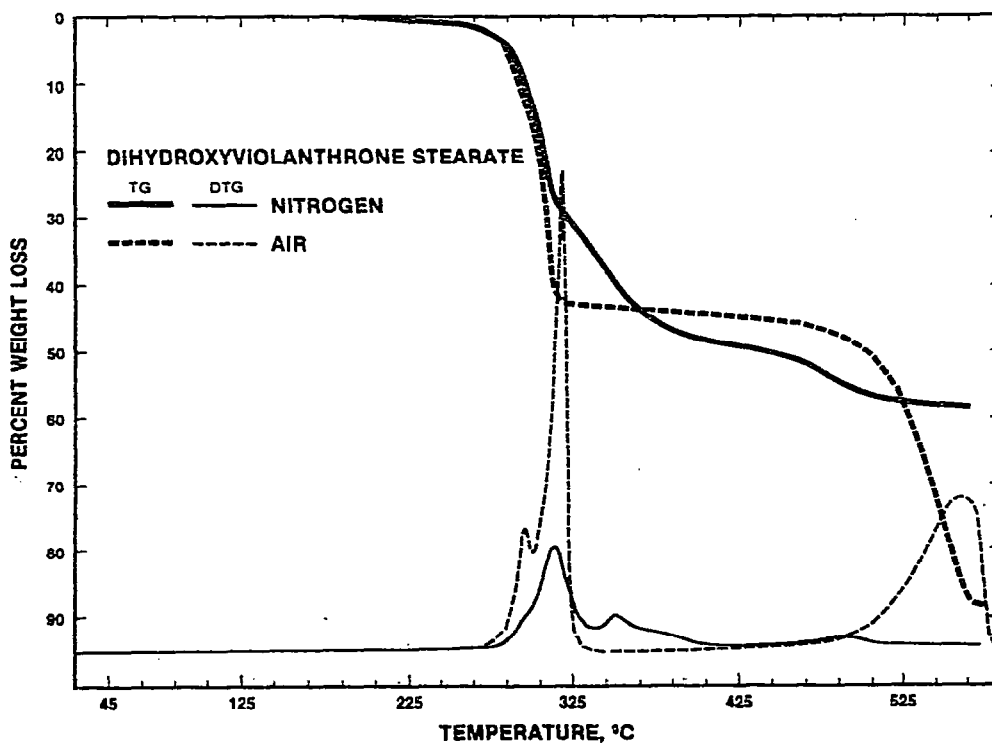Fig. 1. Thermal curves of dihydroxyviolanthrone. Heating rate: $10°C$ min^{-1}.

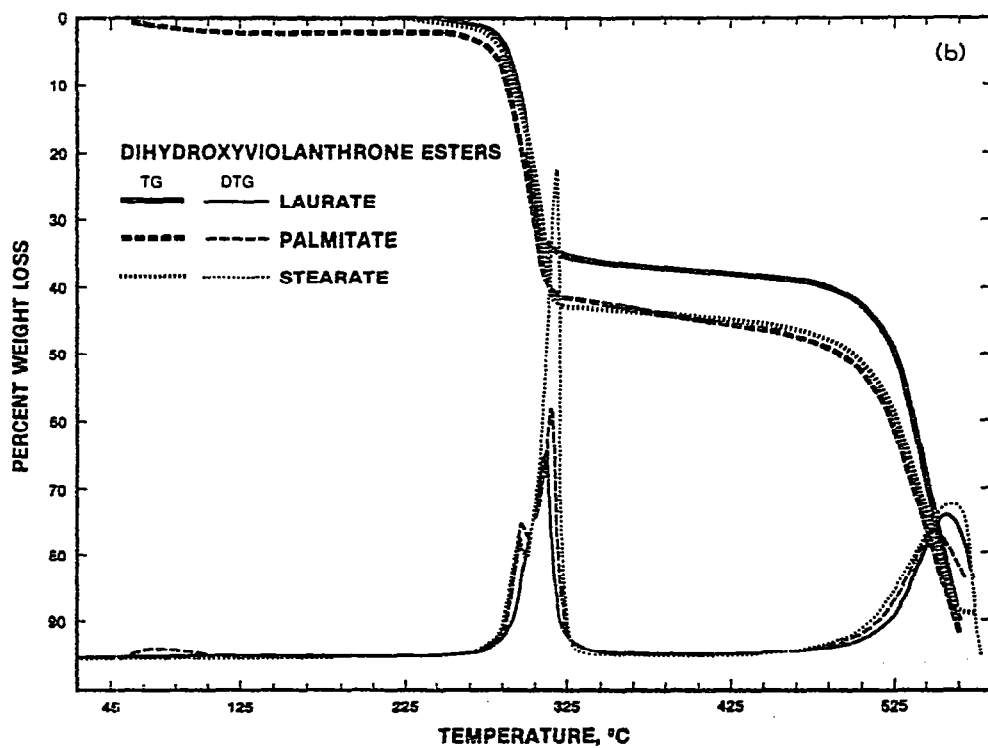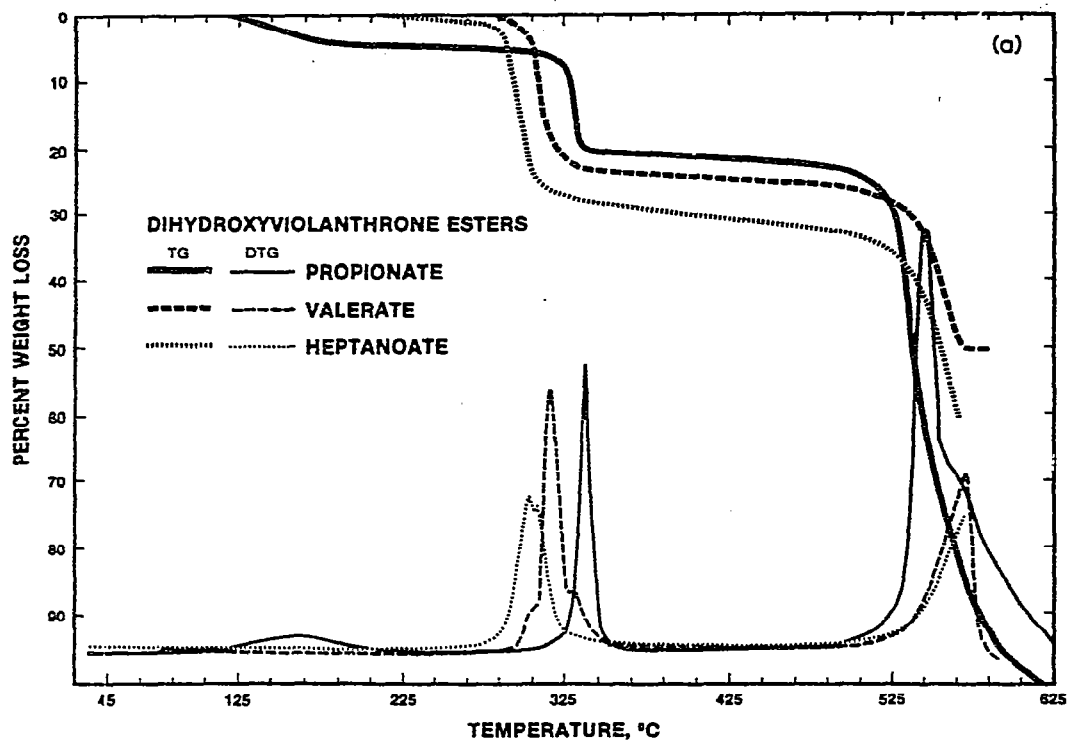Fig. 2. Thermal curves of dihydroxyviolanthrone stearate. Heating rate: $10°C$ min^{-1}.

Fig. 3. Thermal curves of dihydroxyviolanthrone esters in air. Heating rate: 10°C min^{-1}.

TABLE I

DTG peak temperatures for the decomposition of dihydroxyviolanthrone esters in an air atmosphere

Compound	Number of C-atoms in ester chain	DTG peak temperatures (°C)	
		Pyrolysis	Thermo--oxidation
Dihydroxyviolanthrone	0		547
propionate	3	332	571
valerate	5	311	568
heptanoate	7	297, (302) [a]	568
laurate	12	306, (298) [a]	570
palmitate	16	309, (289) [a]	550
stearate	18	311, (289) [a]	560

[a] Minor peak or shoulder.

stability towards high temperature thermo-oxidation and minimum stability towards low temperature pyrolysis. The low temperature process is influenced by chain length more strongly than the high temperature process.

The effect of atmosphere on volatilization and of chain length on stability both suggest that the lower temperature reaction represents the volatilization of the aliphatic part of the molecule. In the range from C_3 to C_7, the peak temperature of
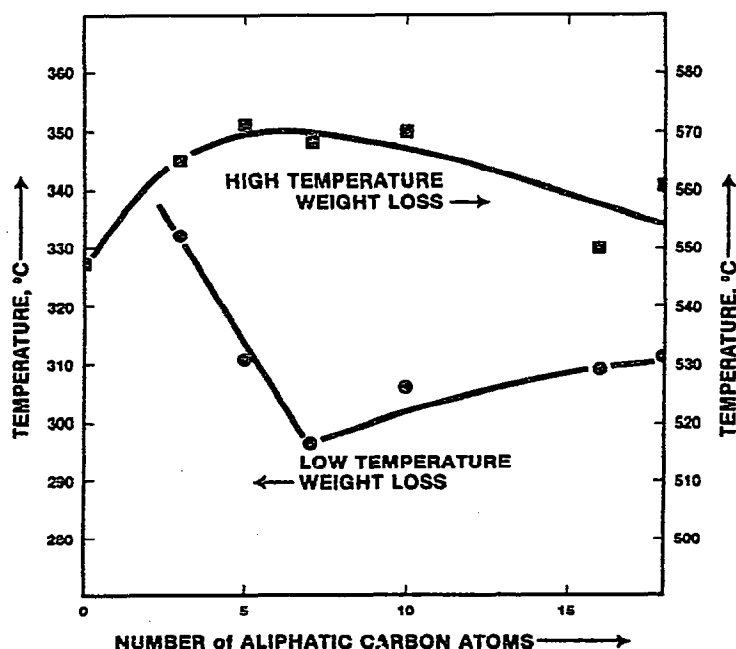

Fig. 4. Plot of decomposition temperatures of dihydroxyviolanthrone esters vs. number of carbon atoms in ester chain. ⊕, Low temperature process, left-hand scale; ▨, high temperature process, right-hand scale.

this process shows a steep linear decrease, while the higher esters show a slight increase in stability. This behavior indicates that the decomposition does not occur by way of a scission of the ester linkage. If the breaking of the ester bond were rate-limiting, the decomposition temperature should be largely independent of chain length. Since this is not the case, one must assume that volatilization occurs via random scission of the hydrocarbon chain. With increasing chain length, the number of possible sites for attack, and thus the overall rate of decomposition, are increased. However, this rate of primary attack eventually reaches a point where it is no longer rate-determining, and the volatilization of the scission products becomes the slowest step.

This interpretation is supported by the kinetics of decomposition under isothermal conditions. As shown in Fig. 5, the weight loss of the stearate ester is linear with time over more than 80% of the decomposition. Zero order kinetics characterize a weight loss process with the rate limited by volatilization of the decomposition products. According to Fig. 6, the temperature dependence of the volatilization rate can be accommodated by the Arrhenius equation with an activation energy of $E = 22.2$ kcal mole^{-1}.

On the other hand, isothermal volatilization curves for the short chain propionates are sigmoidal, with pronounced induction periods, Fig. 7. The much higher activation energy of $E = 87.9$ kcal mole^{-1}, Fig. 8, which is obtained from the temperature dependence of the maximum volatilization rate, confirms the change in the rate-limiting step.
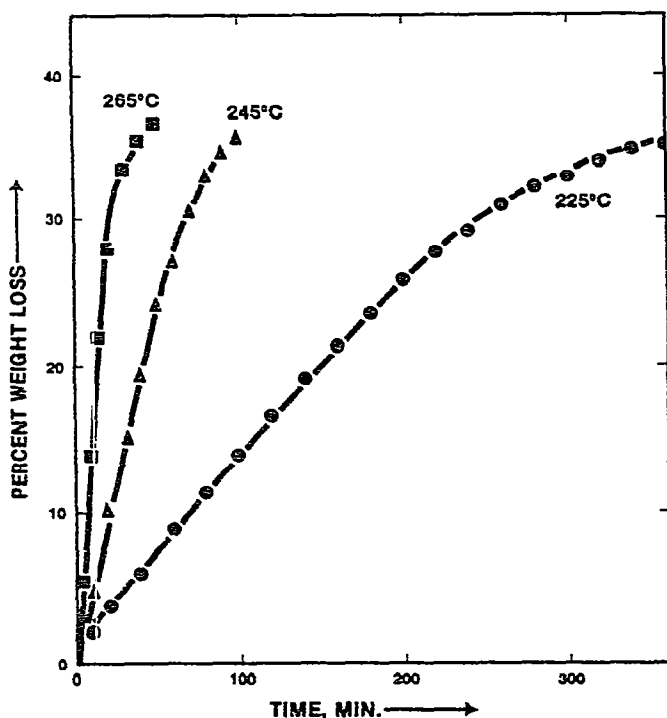

Fig. 5. Isothermal decomposition curves of dihydroxyviolanthrone stearate ester; air atmosphere.
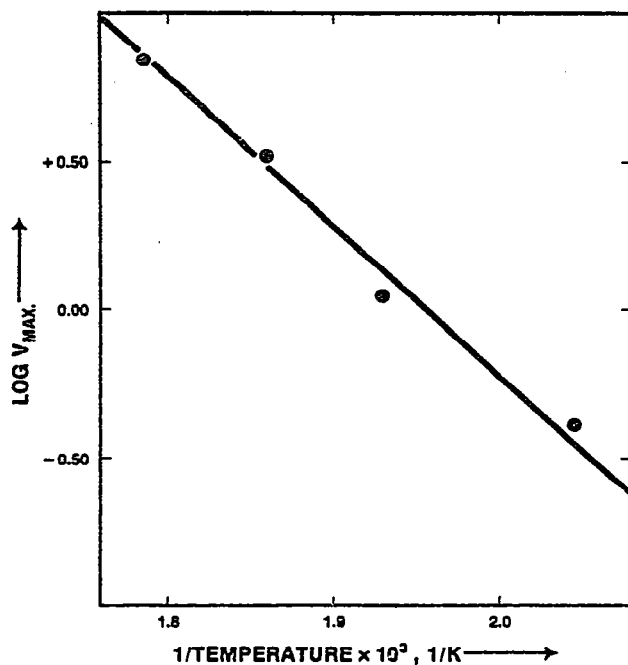
Fig. 6. Arrhenius plot for the volatilization of dihydroxyviolanthrone stearate ester.

If the assignment of the lower temperature weight loss process to the volatilization of the aliphatic part of the molecule is correct, the weight loss should correlate with the weight of the ester side chain. Assuming dihydroxyviolanthrone as the non-volatile fragment, one can calculate the expected weight losses for the various esters and compare them with those obtained experimentally, as shown in Table 2. Plotted in Fig. 9. measured weight losses are seen to agree with those calculated for
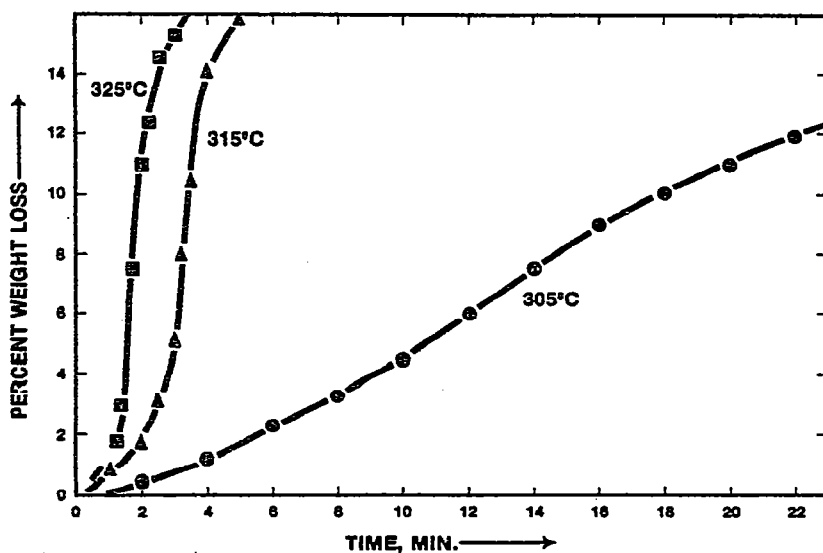

Fig. 7. Isothermal decomposition curves of dihydroxyviolanthrone propionate ester; air atmosphere.
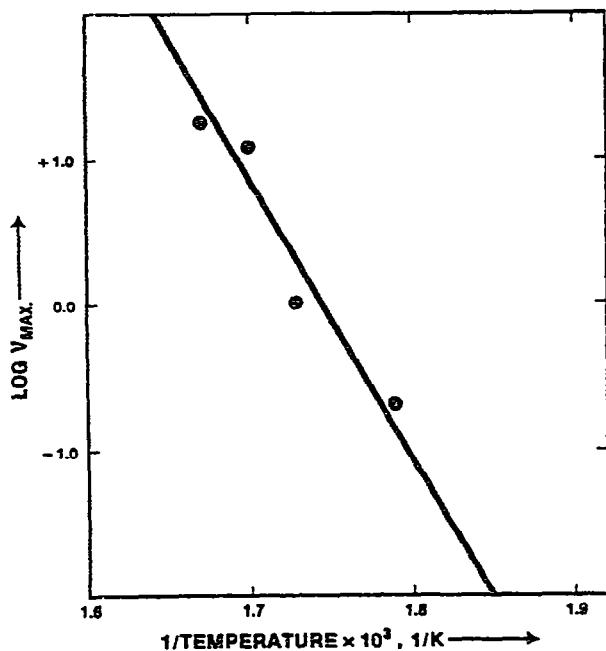
Fig. 8. Arrhenius plot for the volatilization of dihydroxyviolanthrone propionate ester.

the lower molecular weight esters. For the higher molecular weight compounds, the actual weight losses are smaller than the calculated ones.

This suggests that, in the latter case, the aliphatic decomposition products are partially incorporated in the pyrolytically stable residue. This residue is likely to have a highly cross-linked configuration, with large aromatic domains related to the dihydroxyviolanthrone structure. In agreement with the observed behavior, this type of structure is expected to be thermally very stable under non-oxidizing conditions. Thermo-oxidative degradation, however, should take place at high enough tempera-

TABLE 2

Calculated and actual lower temperature weight loss of different dihydroxyviolanthrone esters

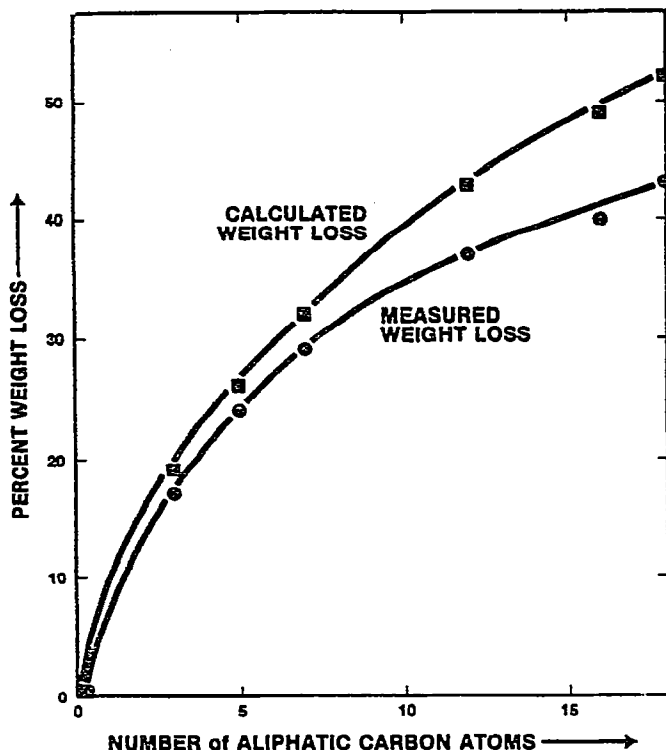| Compound	Number of C-atoms in ester chain	Lower temperature volatile fraction	
		% Calculated	% Measured
Dihydroxyviolanthrone			
propionate	3	19	17
valerate	5	26	24
heptanoate	7	32	29
laurate	12	43	37
palmitate	16	49	40
stearate	18	52	43

Fig. 9. Measured and calculated low temperature weight loss for different dihydroxyviolanthrone esters.

tures which again is in accordance with the experimental results.

To assess the effect of chain branching in the aliphatic portion of the dihydroxyviolanthrone ester on its thermal stability, the thermal curves of the t-butyl acetyl ester was measured both in air and in nitrogen. In a nitrogen atmosphere, a weight loss process of 22% was observed, which agrees with the calculated value of 29%. This suggests that the general thermal decomposition pathway is not affected by the introduction of branching. However, comparing the DTG peak temperatures of 339°C (minor peak) and 347°C with the data in Table 1, it is seen that the branched ester possesses a higher stability than any of the straight chain compounds. In an air atmosphere, complete volatilization occurs above 500°C, which again is in accordance with the decomposition behavior of the straight chain esters.

CONCLUSIONS

(1) Volatilization of free dihydroxyviolanthrone is only possible by a thermo-oxidative pathway. Volatilization under purely pyrolytic conditions does not occur.

(2) For dihydroxyviolanthrone esters of straight chain alkanoic acids, a pyrolytic low temperature decomposition followed by a higher temperature thermo-oxidation is observed.

(3) The low temperature process is influenced by chain length more strongly than the high temperature process. The C_7 ester shows maximum stability towards high temperature thermo-oxidation and minimum stability towards low temperature pyrolysis.

(4) The effect of atmosphere on volatilization and of chain length on stability both suggest that the lower temperature reaction represents the volatilization of the aliphatic part of the molecule.

(5) The general thermal decomposition pathway is not affected by the introduction of branching in the aliphatic portion of the dihydroxyviolanthrone ester. However, the branched ester possesses a higher stability than any of the straight chain compounds studied.

REFERENCES

1 E. Klingsberg, Am. Chem. Soc. Div. Pet. Chem. Prepr., 24 (1980) 519.