

The thermal behaviour of simple aromatic organic compounds with AlCl_3 as additives

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Abstract

The differential thermal analysis (DTA) of a number of simple aromatic organic compounds with the addition of AlCl_3 in different mole ratios allowed the melting and boiling point peaks of the composite samples to be satisfactorily detected. Further, the heats of fusion of the composite samples could be calculated from the endothermic peak area of the melting reaction. The heat of fusion was found to be increased by the addition of AlCl_3 , indicating the consequent increase of the activation energy and hence of the graphitizing power. Thermogravimetric analysis (TGA) of the samples supported the above findings to some extent.

Keywords: Activation energy; Chain-stripping; Cross-linking; Heat of fusion; Mesophase

1. Introduction

Under heat treatment, a substance may undergo structural changes due to dehydration, transition from one crystalline form to another, destruction of the crystalline lattice, oxidation, decomposition, etc. The DTA curve of a substance indicates these changes as a function of temperature.

From the DTA study of a variety of organic compounds it has been found that, in graphitizable materials, endothermic initial processes of transformation are typical, with values of the effective activation energy exceeding 252 kJ mol^{-1} , whereas for non-graphitizable material exothermic initial processes of transformation are observed, with low values of activation energy of $\approx 84 \text{ kJ mol}^{-1}$ [1].

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The DTA has also been employed by Hossain and Dollimore [2] and Hossain and Podder [3] to locate the temperature intervals of mesophase formation as a precursor to graphitization. The carbonaceous mesophase usually appears in the temperature range 623–873 K with the formation of spherules, coalescence and a mosaic texture of optical anisotropy.

In the present investigation, an attempt has been made to study the thermal behaviour of simple aromatic organic compounds with AlCl_3 as additive. DTA and TGA of the samples have been carried out to assess the degree of graphitization.

2. Experimental

2.1. Sample preparation

Pure anthracene (99%, Merck analytical grade) and phenanthrene (99.9%, BDH) were intimately mixed with AlCl_3 in different mole ratios. Pyrolysis of the composite samples was then carried out by sealed tube techniques. During pyrolysis the pressure inside the sealed tube increased, primarily because of the emission of H_2 and hydrocarbon gases. The pyrolysed sample was collected by opening the sealed tube within a safety box to avoid blow-out or explosion due to the high pressure inside.

Partially carbonized samples which had not yet undergone the prolonged heating to cause them to pass through the carbonaceous mesophase were chosen for DTA and TGA. The partial carbonization of a sample could be ascertained by viewing it through a polarized-light microscope using the sensitive tint technique [4].

2.2. DTA and TGA of samples

The experimental details of DTA and TGA have been described in the literature [2, 5, 6].

The samples were subjected to DTA and TGA using a Thermal Analysis Station TAS-100 manufactured by Rigaku Corporation, Japan. The heating rate was maintained at 10 K min^{-1} . As the DTA curves of the composite samples showed initial endothermic peaks for melting, the heat of fusion of the samples was evaluated from the area covered by the peaks [7, 8]. Taking the heat of fusion values for benzoic acid as a standard, the heat of fusion values for all other samples were calculated. TGA was used for quantitative analysis of the samples.

3. Results and discussion

The DTA curves of partially carbonized anthracene and phenanthrene mixed with AlCl_3 in different mole ratios are presented in Figs. 1 and 2. In the DTA curves, a common feature is the presence of an initial large endotherm due to melting of the tarry substance. The second large endotherm corresponds to the boiling point of the

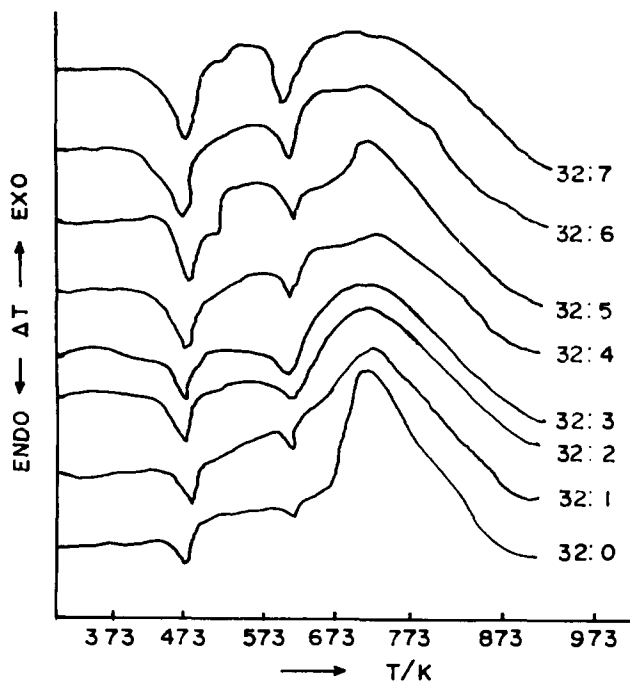


Fig. 1. DTA curves of anthracene with AlCl_3 in different mole ratios.

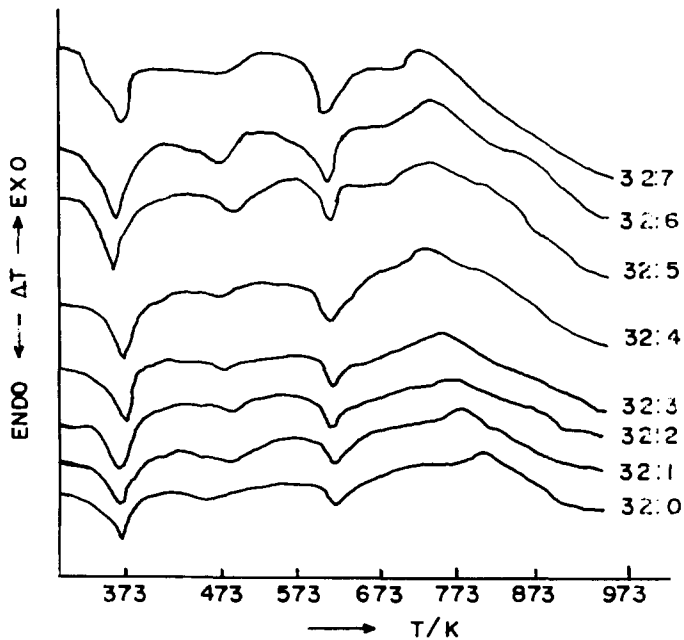


Fig. 2. DTA curves of phenanthrene with AlCl_3 in different mole ratios.

substance, and these two endotherms are followed by small fluctuations in the curve before a smooth curve is re-established. The temperature at which the fluctuations cease just before the smooth curve, is merely the temperature of complete coalescence in the case of the carbonaceous mesophase. The fluctuations may arise through the formation of hydrogen and hydrocarbon gases within the samples during pyrolysis. This could result in the sample being lifted away from the thermocouple momentarily, thus causing a small peak in the curve. This process may then repeat itself until the sample has decomposed to produce a mosaic exhibiting complete coalescence of the mesophase.

The TGA curves of the same samples are presented in Figs. 3 and 4. The weight losses of the samples start from ≈ 373 K and substantially continue up to the coalescence temperature, owing to the elimination of hydrogen and hydrocarbon gases. The TGA results show that the carbon yield is increased by the addition of AlCl_3 , which is supported by the assumption of Blayden et al. [9].

The DTA curves show that the initial large endotherm gradually increases in size with the addition of AlCl_3 . This increase in the initial large endotherm indicates an increase in the heat of fusion, which in turn indicates the consequent increase of activation energy [10] and hence of graphitizing power. The heats of fusion of

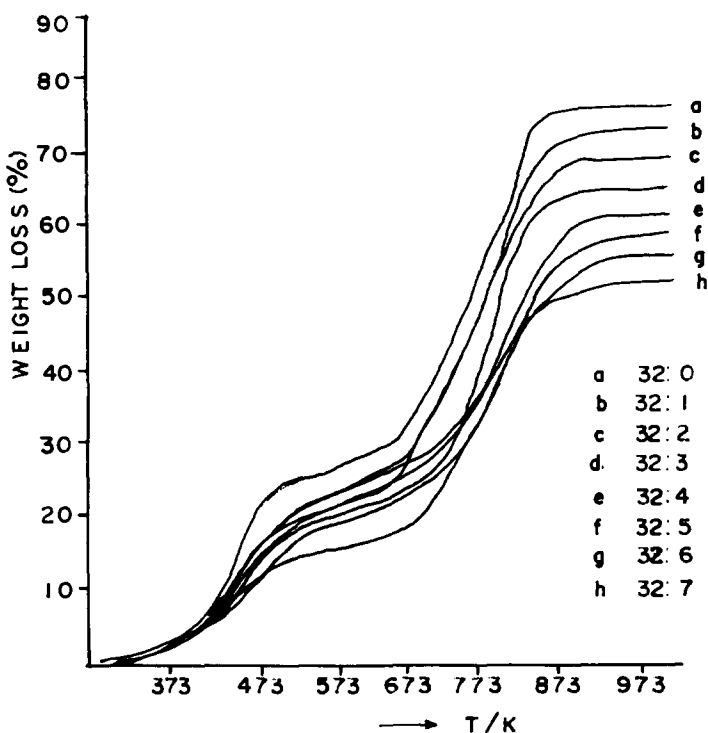


Fig. 3. TGA curves of anthracene with AlCl_3 in different mole ratios.

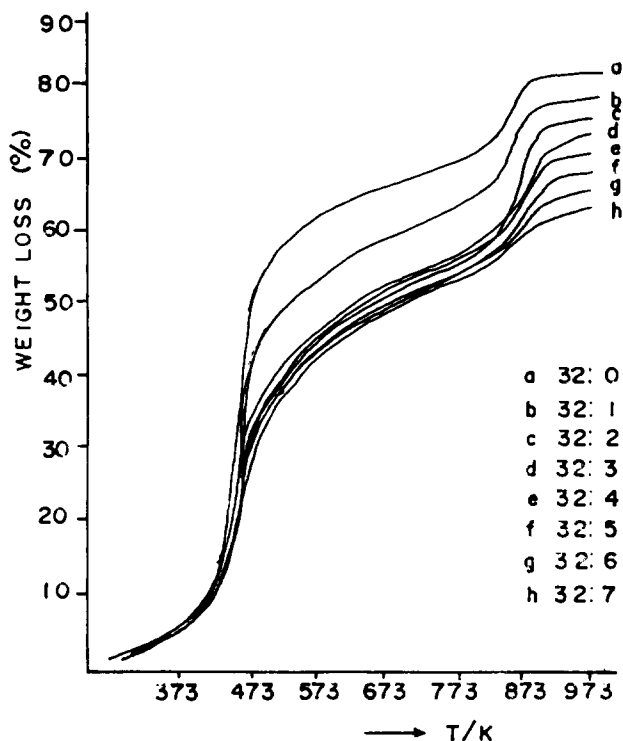


Fig. 4. TGA curves of phenanthrene with AlCl_3 in different mole ratios.

composite samples calculated from the first endothermic peak area of each DTA curve are shown graphically in Fig. 5.

The function of AlCl_3 is to cause chain-stripping and associated reactions, allowing planar distribution of the aromatic rings, an essential prerequisite for the formation of graphite.

4. Conclusions

The DTA curves of anthracene and phenanthrene (Figs. 1 and 2) have relatively broader initial endothermic peaks with increasing amounts of AlCl_3 . Broadening of the initial endotherm means that the heat of fusion and thus the activation energy gradually increase with increase in the amount of AlCl_3 (Fig. 5). This indicates that carbons obtained from pure aromatic samples in the presence of AlCl_3 have relatively higher graphitizing power.

As the amount of AlCl_3 added to the sample is gradually increased, the mesophase interval becomes significantly shorter, which indicates the increasing degree of graphitization.

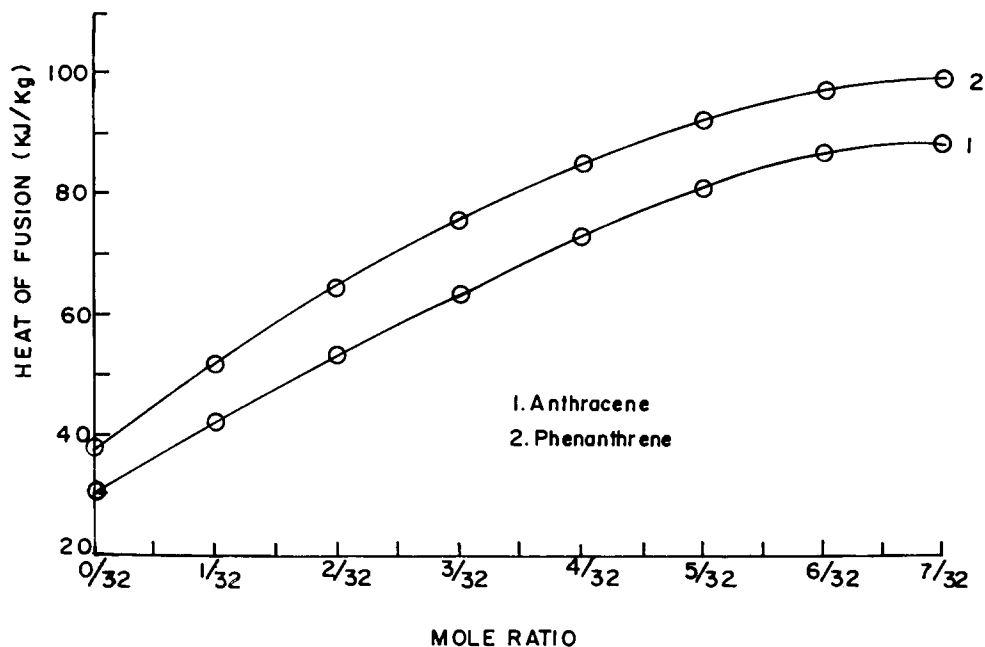


Fig. 5. Variation of heat of fusion with mole ratio of AlCl_3 .

The TGA curves of the samples (Figs. 3 and 4) predict the increasing yield of carbon with the increase in the amount of AlCl_3 . The greater the yield of carbon, the greater will be the degree of graphitization.

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