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OXIDATIVE PROFILES OF SOME AUSTRALIAN OIL SHALES BY THERMAL ANALYSIS AND INFRARED SPECTROSCOPY

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ABSTRACT

Thermogravimetric and derivative thermogravimetric oxidative profiles were obtained for a number of Australian oil shales and kerogen concentrates heated in a dynamic air atmosphere. Evolved gas analysis curves and the associated first derivative curves were obtained for these materials by following the increase in optical absorption of the principal IR bands of gaseous species evolved during linear heating. Thermochemical changes in kerogens were also studied by means of solid-state IR transmission spectroscopy.

Combustion of kerogen occurs in two stages, indicated by two sharply defined DTG peaks. The first stage involves complete or almost complete combustion of aliphatic components to give a char containing aromatic moieties.

Evolved gas analysis and derivative evolved gas analysis curves for sulfur dioxide evolution, used in association with TG–DTG data, provide a means of characterising oil shale in terms of sulfur distribution.

INTRODUCTION

Studies of oil shales using DTA and DSC techniques [1–3] have shown that combustion of indigenous organic matter (kerogen) is a complex multistage process, indicated by broadly overlapping exotherms. Recently, Earnest [4] used TG–DTG oxidation profiles of some American and Australian oil shales to confirm the multistage nature of kerogen combustion in air. In this paper we describe the use of TG–DTG curves, complemented by evolved gas analysis and derivative evolved gas analysis (EGA–DEGA) techniques, to study oxidative breakdown of some Australian oil shales. The results show that, by using optimised amounts of powdered samples in thinly-spread layers, the various stages of oxidation are highlighted by well-resolved DTG peaks with minimal overlap. Changes in the IR spectra of kerogen during combustion can be correlated unambiguously with DTG and DEGA data,

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thus providing a useful means of characterising and comparing the various shales.

EXPERIMENTAL

Specimens of oil shale were obtained from the Condor, Julia Creek, Rundle, Duaringa, Nagoorin and Stuart deposits in Queensland, and from the Glen Davis and Hartley Vale torbanite deposits in New South Wales. After crushing and sieving, a sieved fraction ($-1.4-+0.6$ mm) of each specimen was chosen for analysis. Preliminary experiments showed that ball milling of the sieved fraction led to improved resolution of DTG and DEGA peaks; therefore all other thermal analyses were done using ball milled powdered material. Kerogen concentrates were obtained by treating the powdered oil shales with HCl then HF solutions, followed by filtering, water-washing and vacuum drying. Concentrates obtained from the torbanites contained about 2% or less mineral matter, whereas the Queensland oil shales yielded concentrates containing 5–15% mineral matter, with pyrite as a major mineral component.

TG data were obtained using a Cahn RH electrobalance interfaced to an LSI-11 computer via a 12-bit analogue to digital converter. Temperature was measured with a chromel–alumel thermocouple positioned about 2 mm beneath the sample. DTG curves were derived from TG data by a recursive digital filter in a smoothing routine, as described elsewhere [5]. Optimal resolution of DTG peaks was obtained using thinly spread layers of powdered material containing 15–20 mg kerogen. Platinum sample pans were generally used, although some measurements were made using gold or silica pans to confirm that the pan materials did not exercise a catalytic effect upon the oxidation behaviour.

Infrared spectra of evolved gases showed that combustion of the Queensland kerogen samples yields carbon dioxide, water vapour and sulfur dioxide, whereas the New South Wales torbanites give only carbon dioxide and water. A JASCO A-302 double beam IR spectrophotometer was used to follow the increase in optical absorption of the principal band of each gas while the shale or kerogen sample was heated at 10 deg min^{-1}.

The IR gas cell was 10 cm long and of 200 cm^3 volume with 50 mm NaCl windows. The sample (containing 5–10 mg kerogen) was spread on an open platinum pan inside a microfurnace. Sample pan and furnace were integrated as a demountable assembly, situated inside the gas cell but outside the sample beam.

Solid-state IR spectra for kerogens and kerogen residue samples were obtained using the pressed KBr disc technique. Each kerogen residue was obtained by linear heating to a temperature corresponding to the completion of a thermogravimetric event, as indicated by the DTG curve.

RESULTS AND DISCUSSION

TG–DTG oxidative profiles are given in Fig. 1 for various shales and kerogen concentrates. Certain DTG peaks can be related to the inorganic mineral components of the oil shales. For example, Julia Creek oil shale exhibits a major weight loss between 600 and 800°C owing to the decomposition of the principal mineral phase, calcite. All the Queensland shales (apart from one Julia Creek specimen) exhibit a DTG peak at about 440°C which is confirmed by EGA–DEGA measurements (see below) as arising from oxidation of pyrite. This mineral is difficult to remove completely by acid demineralisation, so some of the kerogen concentrates also exhibit a 440°C DTG peak, although much diminished. Pyrite or carbonates are not present in the NSW torbanite specimens, and the TG data for these materials are entirely due to combustion of organic matter. By comparing oxidative profiles of the various shales and their corresponding kerogen concentrates, it can be seen that, in every case, combustion of kerogen occurs in two distinct stages, all within the temperature range 200–600°C.

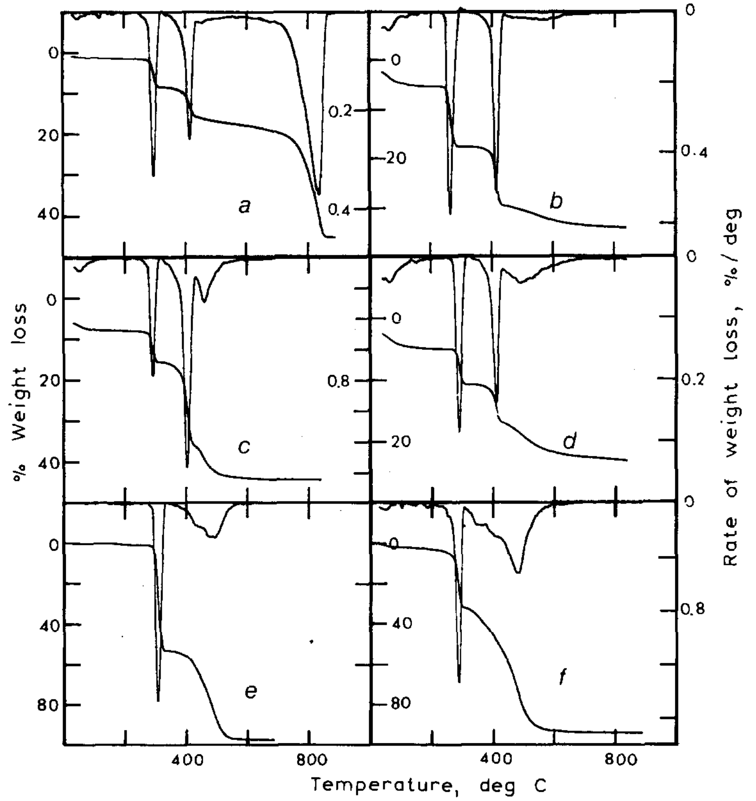

Fig. 1. TG and DTG curves for oil shales and kerogen concentrates heated at 10 deg min^{-1} in air. a, Julia Creek oil shale; b, Rundle oil shale; c, Nagoorin oil shale; d, Condor oil shale; e, Hartley Vale kerogen concentrate; f, Duaringa kerogen concentrate.

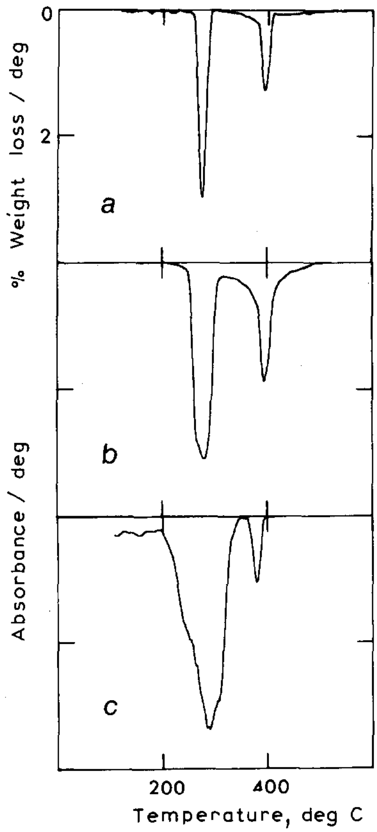

Fig. 2. Oxidative profiles for Julia Creek kerogen concentrate heated at 10 deg min^{-1} in air. a, DTG curve; b, DEGA curve for evolution of CO_2 measured at 2359.2 cm^{-1}; c, DEGA curve for evolution of H_2O measured at 1509.3 cm^{-1}.

TG–DTG curves for the various kerogen concentrates fall into two categories; the NSW torbanites and the Duaringa kerogen form one category and the other Queensland specimens of Julia Creek, Condor, Stuart and Nagoorin form the other. All kerogen concentrates derived from the Queensland shales (apart from the Duaringa specimen) give DTG curves that are qualitatively alike, with two prominently sharp DTG peaks at 270 and 375°C. In contrast, combustion of the Duaringa and torbanite kerogens is denoted by a sharp DTG peak at 315°C, with a broader peak at 500°C.

EGA–DEGA curves are useful for elucidating the different stages of oxidation. As an example, Fig. 2 gives DEGA profiles for Julia Creek kerogen together with the corresponding DTG curve; from these data it can be seen that CO_2 and H_2O are evolved during both oxidation stages. However, although CO_2 and H_2O are produced in roughly equal amounts in the first stage, CO_2 is the major product of second-stage combustion. These results indicate that the first stage involves kerogen components of a relatively low C : H ratio, consistent with reactions in which aliphatic groups

TABLE 1

Infrared spectra of kerogens

Band frequency (cm^{-1})	Assignment
3400	O–H stretch
2930	asym. stretch, CH_2 alkyl
2860	sym. stretch, CH_2 alkyl
1700	C=O stretch, ester, aldehyde, -COOH
1620	C–C vibration of aromatic rings
1465	asym. band of alkyl CH_3 and CH_2 groups
1375	mainly sym. band of CH_3 groups

predominate. The high ratio of evolved $CO_2:H_2O$ for the second stage, although suggestive, does not provide firm proof that combustion of aromatic components is dominant; elemental carbon may also be present.

The differences in oxidative behaviour observed for the two categories of kerogen reflect compositional differences, as indicated by the solid-state IR spectra of kerogen concentrates. The Duaringa and NSW torbanite specimens display a moderately intense band at 720 cm^{-1}, due to CH_2 rocking vibrations of non-cyclic hydrocarbons containing more than four contiguous CH_2 groups, whereas the other kerogens do not. Although IR spectra of all the kerogens are otherwise the same, in the sense that they show the same principal bands, they differ substantially in band intensities.

Table 1 lists the principal frequencies, together with their assignments.

Figures 3(a–d) compare IR spectra of Hartley Vale, Duaringa, Julia Creek and Nagoorin kerogens as examples of each category. The aliphatic content of Hartley Vale material is noticeably higher than that of the other three kerogens, as shown by the substantially greater intensity of alkane bands at 2930, 2860, 1455 and 1375 cm^{-1}, together with a relatively weak aromatic band at 1620 cm^{-1}; there are, however, fewer carboxylic groups, as indicated by lower relative intensities of the O–H band at 3400 cm^{-1} and the C=O stretching band at 1700 cm^{-1}. In contrast, the Nagoorin specimen is the most aromatic of the four materials, having weak alkane vibrational stretching bands and a correspondingly more intense aromatic band at 1620 cm^{-1}. The other kerogen specimens are intermediate between these two extremes in terms of aliphatic : aromatic ratio.

Figures 3(e,f) show the IR spectra of Julia Creek and Hartley Vale kerogens after completion of the first oxidation stage. It can be seen that alkane bands are no longer evident for Julia Creek material, and are drastically reduced in the spectrum of Hartley Vale kerogen residue. Bands arising from O–H, C=O, and aromatic vibrations are prominent, however. These results corroborate the EGA–DEGA data, confirming that, for the most part, the first oxidation stage involves combustion of aliphatic components and confirm the view that second-stage oxidation is combustion of a

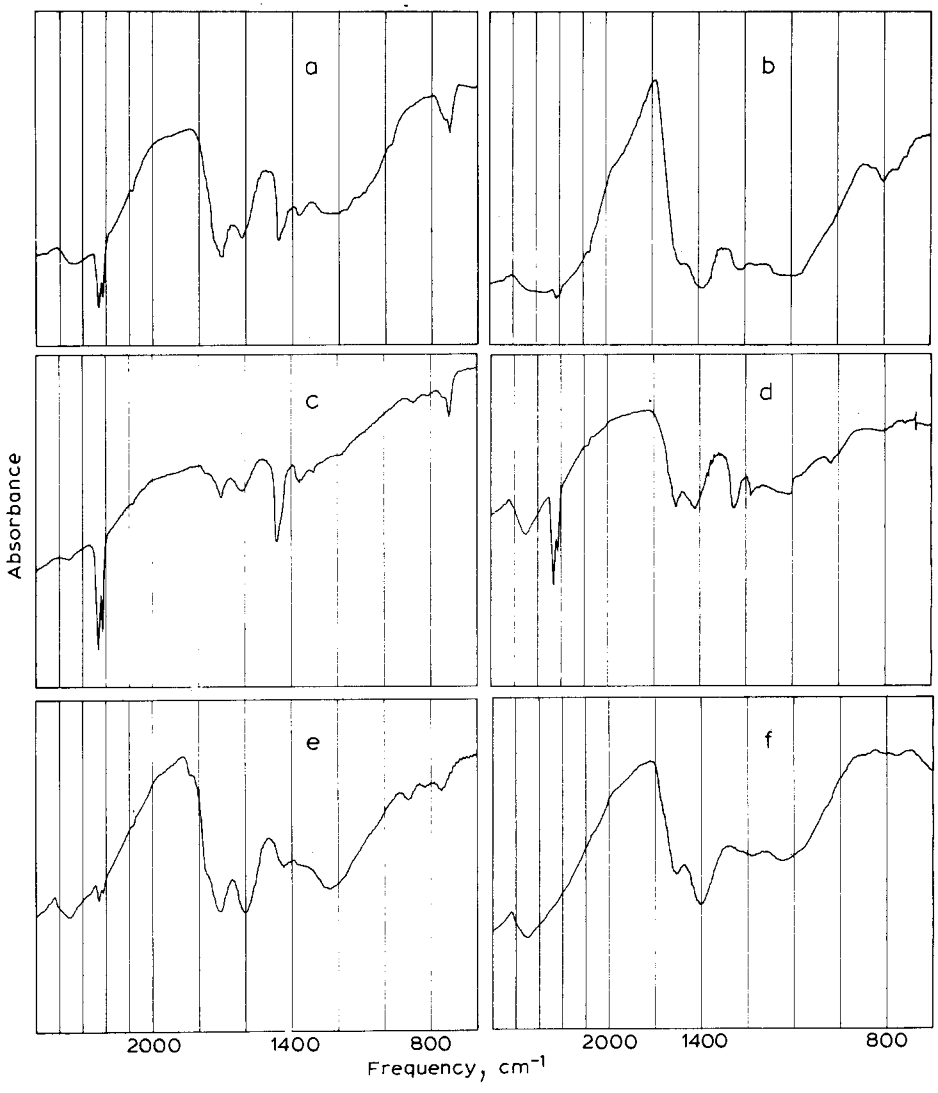

Fig. 3. Solid-state infrared transmission spectra of kerogens and kerogen residues. a, Duaringa kerogen concentrate; b, Nagoorin kerogen concentrate; c, Hartley Vale kerogen concentrate; d, Julia Creek kerogen concentrate; e, Hartley Vale kerogen residue formed by heating through the first oxidation stage at 10 deg min^{-1} in air; f, Julia Creek kerogen residue formed by heating through the first oxidation stage at 10 deg min^{-1} in air.

char containing aromatic moieties and carboxylic groups. Similar results were observed for the other kerogen specimens.

It should be pointed out that first-stage oxidation does not represent gas-phase combustion of volatiles generated by pyrolytic breakdown of kerogen. This can be seen by comparing TG–DTG profiles for pyrolysis in nitrogen with the corresponding oxidative curves. In Fig. 4 for example, DTG curves for pyrolysis of Condor and Hartley Vale kerogens in nitrogen

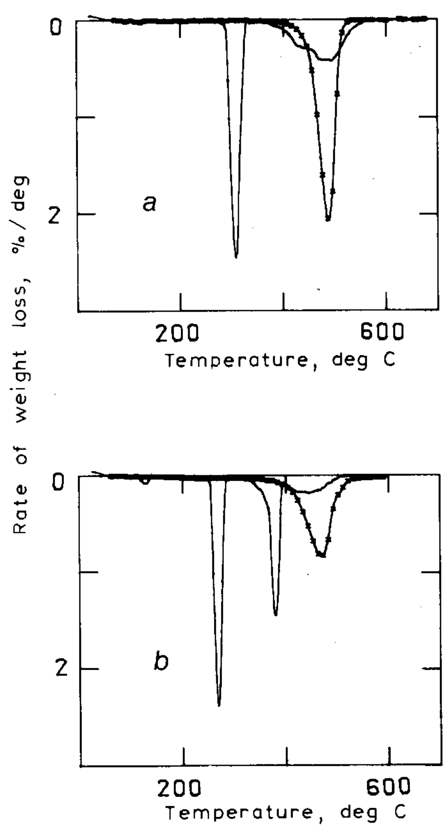

Fig. 4. Oxidative (————) and pyrolytic (—×—×—) DTG profiles compared for Hartley Vale and Condor kerogen concentrates. a, Hartley Vale kerogen; b, Condor kerogen.

are superimposed on the corresponding oxidation curves; clearly, the pyrolytic decomposition of these kerogens occurs well above the temperature range for first-stage oxidation. Similar behaviour was observed for the other kerogens; so, within the experimental conditions of our thermal analysis, oxidation of kerogen occurs via a gas–solid reaction mechanism.

The superposition of a DTG oxidation curve on the corresponding DEGA curve for SO_2 evolution offers another useful application of thermal analysis for characterising oil shales and establishing the distribution of sulfur in a shale sample. This is illustrated in Fig. 5 for Condor and Nagoorin materials. A DEGA peak at about 440°C for Condor kerogen concentrate is undoubtedly due to oxidation of pyrite, since it coincides with the DTG peak at 440°C and no CO_2 is evolved during this third oxidation stage. Sulfur dioxide is evolved during the first stage of oxidation, but none in the second stage. From these results we conclude that organic sulfur is associated entirely with the aliphatic component for Condor kerogen.

SO_2 is also evolved during first-stage oxidation of the Nagoorin material but, from curves c and d of Fig. 5, it can be seen that a second, broader DEGA peak covers both second and third-stage oxidation. We conclude therefore, that in the Nagoorin specimen, organo–sulfur groups are associ-

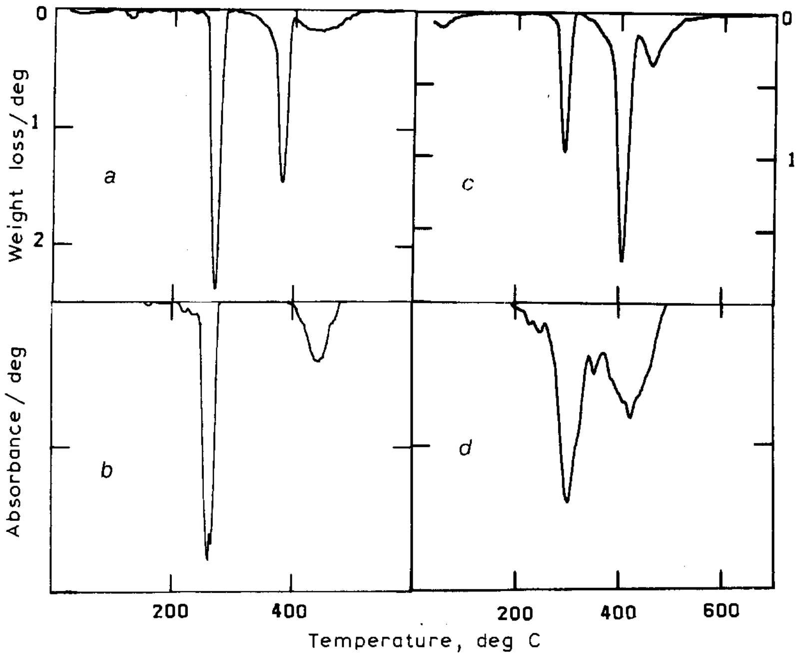

Fig. 5. DTG oxidative profiles compared to DEGA oxidation profiles for SO_2 measured at 1361.7 cm^{-1}. a, DTG curve for Condor kerogen concentrate (ash content 12%); b, DEGA (SO_2) for Condor kerogen concentrate; c, DTG curve for Nagoorin oil shale (ash content 10%); d, DEGA (SO_2) for Nagoorin oil shale.

ated with aromatic components as well as aliphatic components of the kerogen.

The results show that the combination of thermoanalytical techniques and IR spectrophotometry offers a useful means of defining and comparing various oil shales. The properties of the specimens that we have described may not of course be typical of the shale deposits in question, but there is no doubt that the techniques can be profitably developed to study oil shale samples which are geologically and petrographically well defined.

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