

APPLICATION OF PYROLYSIS GAS CHROMATOGRAPHY TO EXAMINATION OF BEHAVIOR IN RETORTING OF VARIOUS OIL SHALES

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ABSTRACT

Stepwise pyrolysis-gas chromatography for oil shales was carried out with special attention being paid to the effect of pyrolysis temperatures, mineral matter and H₂ atmosphere on the product profile. The samples used for this experiment were Colorado (USA), Condor (Australia), Timhadit (Morocco) and Maoming (China) oil shales and their kerogens. In the early stage of pyrolysis, pyrolyzates rich in alkylbenzenes (Condor and Maoming) or prist-1-ene (and pristane in the case of experiment under H₂) (Colorado) were obtained. Timhadit oil shale gave the pyrolyzates rich in thiophene derivatives in its early stage of pyrolysis. In the advanced stage, pyrograms essentially consisting of a series of olefin/paraffin pairs were obtained with all the shales and kerogens investigated. Pyrolyzates became rich in toluene and benzene with increasing the temperature. Hydrogen seemed to be effective in increasing benzene yield at high temperatures. Various types of linkage in kerogen matrix with different bond dissociation energies should give such variations of product distribution with temperature. Mineral matter may not play a significant role in the kerogen decomposition.

INTRODUCTION

Detailed characterization of shale oil is crucial to utilization of oil shale as an industrial raw material. Pyrolysis-gas chromatography

(Py-GC) techniques have been applied widely to the analysis of insoluble organic polymers including kerogens. The ability to control thermal conditions carefully in Py-GC experiments suggests that these techniques should be useful in examining the yield and product profile depending on pyrolysis condition as a means of evaluating oil shale retorting behavior.

The work presented here deals with an examination of a Py-GC technique for evaluation of retorting potential of various oil shales. Attention has been focused on the effect of pyrolysis temperature, mineral matters and H₂ atmosphere.

EXPERIMENTAL

Oil shales examined in this study are from Colorado (USA), Condor (Australia), Timhadit (Morocco) and Maoming (China) deposits and their kerogens. Kerogen isolation procedure was reported elsewhere¹). Geologic age, depositional environments and major inorganic components of each oil shale are shown in Table 1 with the atomic H/C ratio of each kerogen.

The equipment for the Py-GC consists of a Chemical Data Systems Pyroprobe 120 attached to a Shimadzu GC-9A with an FID detector. An oil shale (100-200 mesh, 15 mg) or a kerogen sample (5 mg) was inserted into a thin wall quartz tube (1.5 mm in inside diameter and 25 mm in length) which was then placed into the platinum coil of the pyrolysis probe. The platinum coil serves as both a heater and a sensor, permitting a rapid rise in temperature. In this paper, the preset temperature of the Pt filament is defined as the pyrolysis temperature. The actual temperatures of the pyrolysis is estimated to be ca. 150 °C lower than the preset temperature. This instrument seems to yield sufficiently reproducible thermal degradation. The temperature of pyrolysis chamber was kept at 250 °C. Before pyrolysis, the sample was treated at 300 °C for 20 sec to remove volatile matter. The sample was rapidly heated under a 60 ml/min flow of He or H₂, to 600 °C, held at this temperature for 20 sec and then allowed to cool down. The pyrolysate was introduced directly into the gas chromatograph with the carrier gas and analyzed on an OV-1 coated fused silica capillary column (50m x 0.25mm i.d.). The column was heated from 40 to 290 °C with

a heating rate of 5 °C/min. The GC peaks were identified using a Shimadzu mass spectrometer QP 1000. The sample was further heated successively to 650, 700, 800 and finally 900 °C, and the pyrolysate was analyzed in the same way. The sample was held at each temperature for 20 sec and then allowed to cool down.

Table 1. General information for the samples

deposit	geologic age	depositional environments	major inorganic components	H/C for kerogen
Colorado	Eocene	lacustrine	DO, Q, OR, CA, AL	1.54
Condor	Tertiary	lacustrine	Q, KA, IC,	1.30
Timhadit	Cretaceous	marine	DO, CA, Q	1.26
Maoming	NA	lacustrine	Q, KA, GY,	1.24

DO = dolomite = $\text{CaMg}(\text{CO}_3)_2$, CA = calcite = CaCO_3 ,
 IC = iron carbonate,
 KA = kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, Al = albite = $\text{NaAlSi}_3\text{O}_8$,
 OR = orthoclase = KAlSi_3O_8 ,
 GY = gypsum = $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Q = quartz = SiO_2

RESULTS

Fig.1 shows the pyrolysis-gas chromatograms (pyrograms) for the four oil shales heated stepwise to the preset temperature. The pyrograms reveal primarily a homologous series of alkanes from C_1 to C_{30} , and also a 1-alkene series as the peaks immediately before those of the respective alkanes. In all of pyrograms obtained at 600 °C, the abundance of alkylbenzenes are relatively large. Colorado oil shale gives a high yield of prist-1-ene as a distinct major peak. Formation of prist-1-ene is also observed but in much less amount with the other shales. The peaks between the olefin/paraffin pairs on the pyrogram at 600 °C for Timhadit oil shale are largely composed of alkylthiophenes. It is noteworthy that Timhadit oil shale gives the majority of the products in this early stage of pyrolysis.

Pyrolysis at 650 and 700 °C leads to the spectra mainly consisting of a

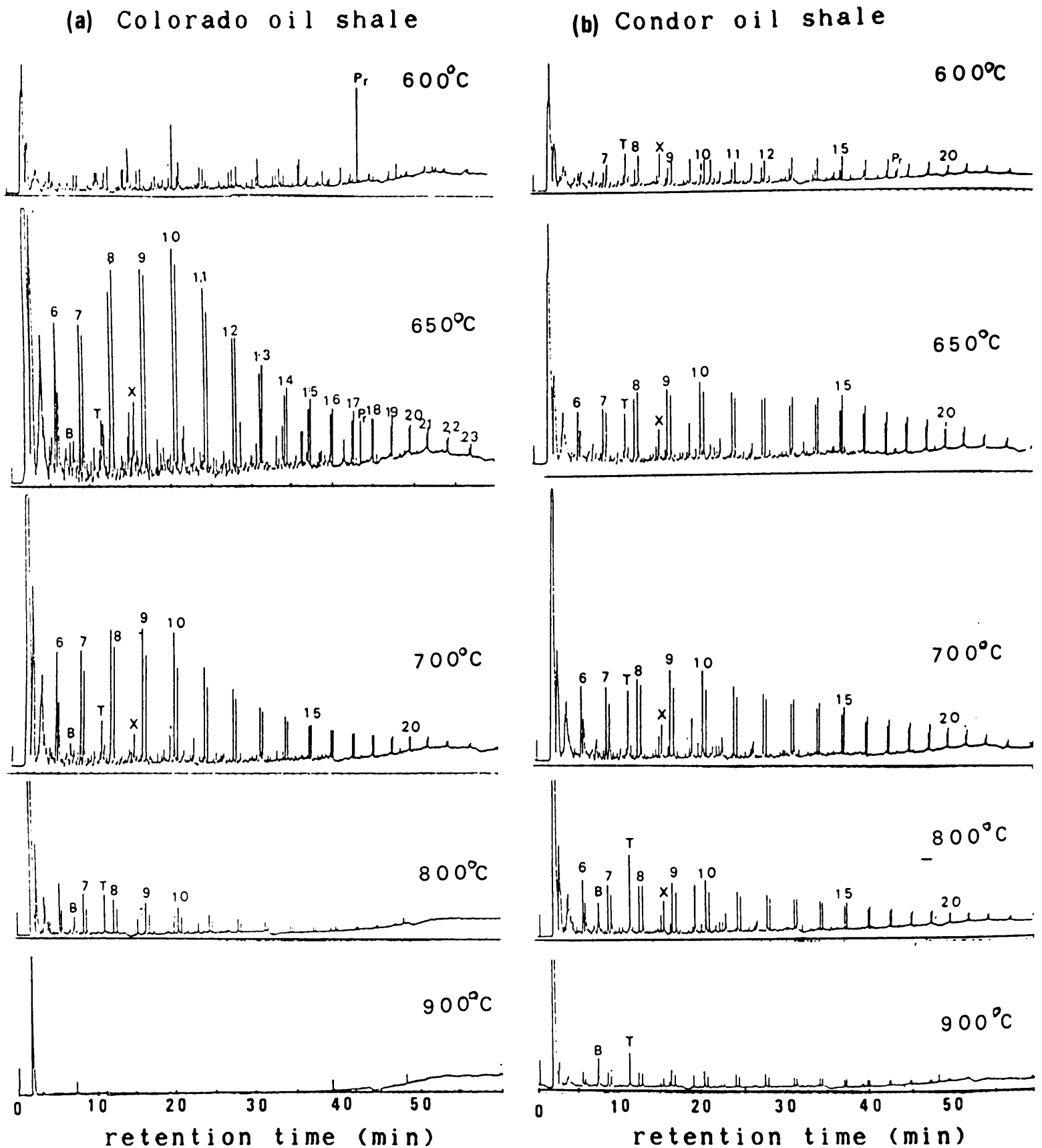


Fig. 1 Variation in product distribution on stepwise pyrolysis of oil shales (under He atmosphere)

Arabic numerals correspond to the carbon numbers of olefin(left) and paraffin(right) pairs; B, T, X and Pr correspond to benzene, toluene, xylenes and prist-1-ene, respectively. Italic numerals indicate thiophene derivatives shown below. Most of unlabelled peaks in pyrograms for Colorado, Condor and Maoming oil shales correspond to alkyl benzenes, and those for Timhadit oil shale correspond to thiophene derivatives.

① 2-methylthiophene, ② 2,4- and/or 2,5-dimethylthiophene,
 ③ 2-isopropylthiophene, ④ 2,3,4-trimethylthiophene.

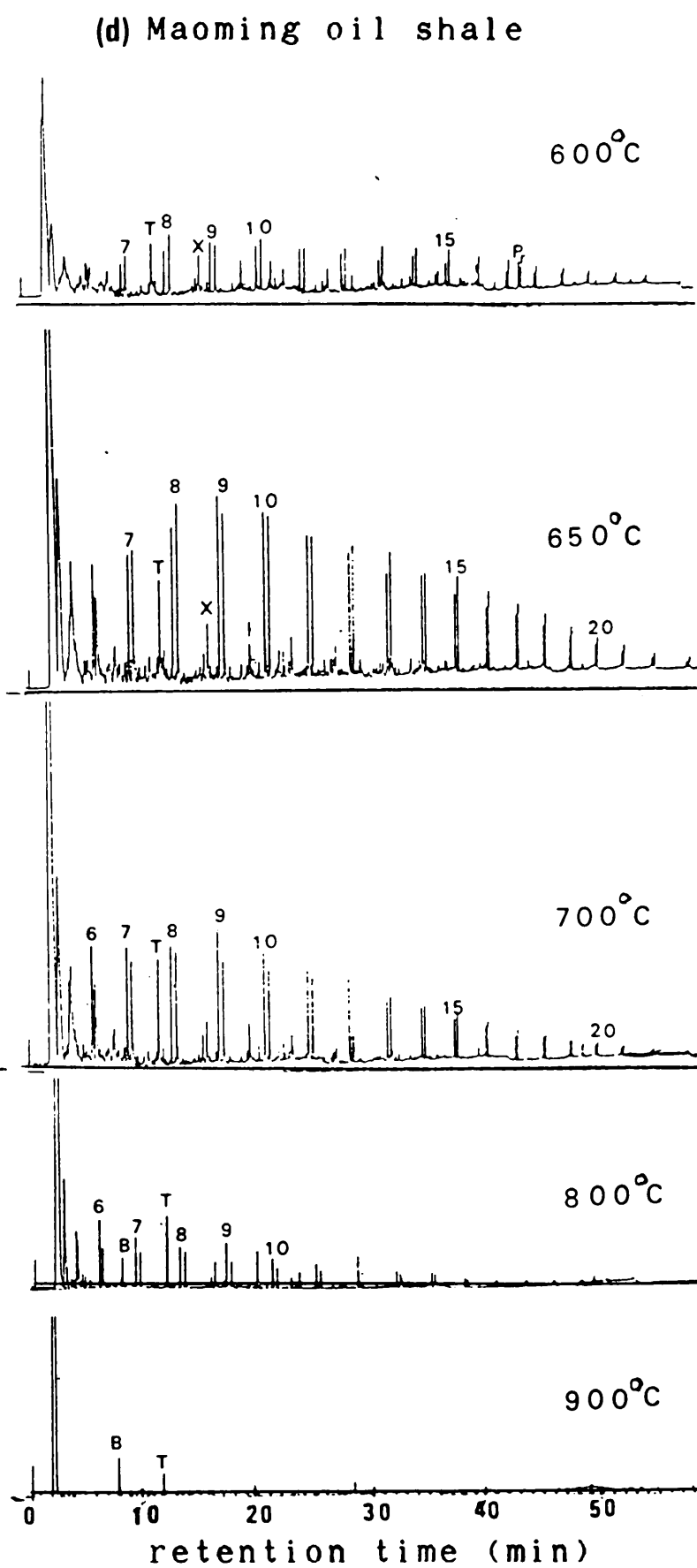
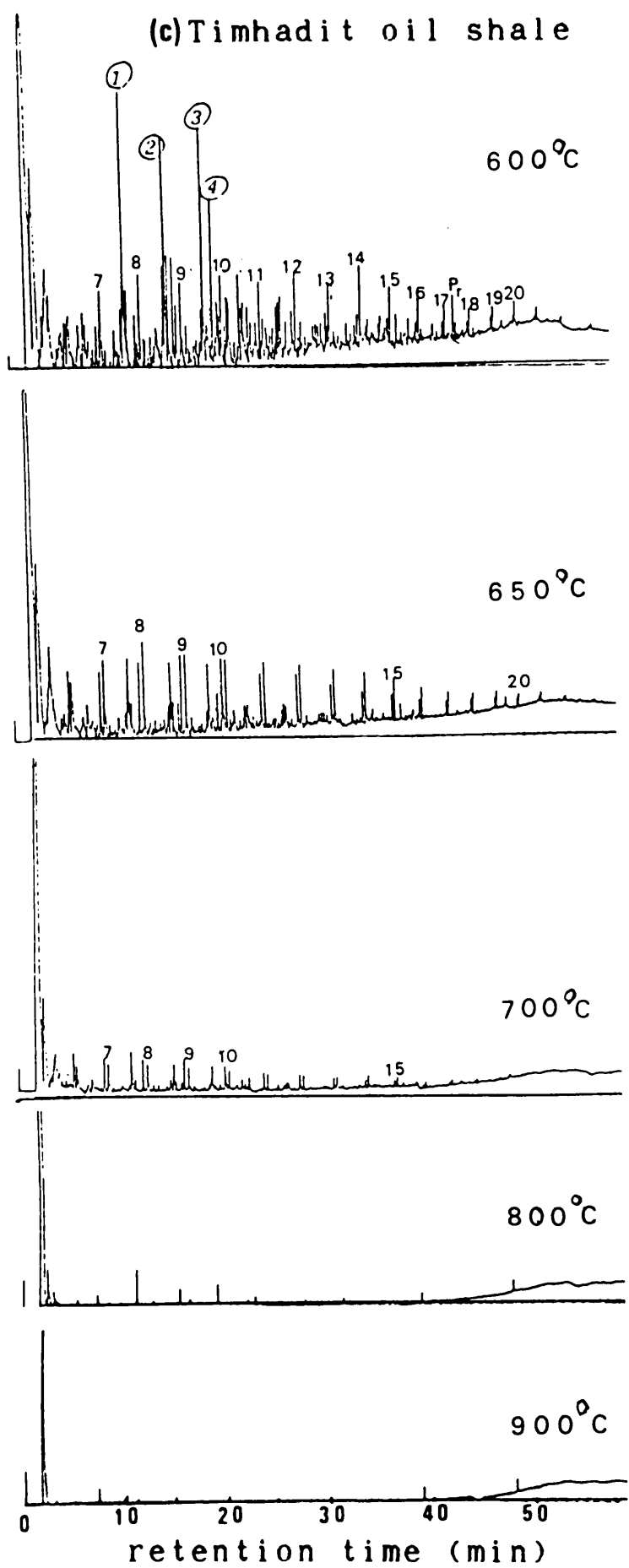


Fig. 1 (continued)

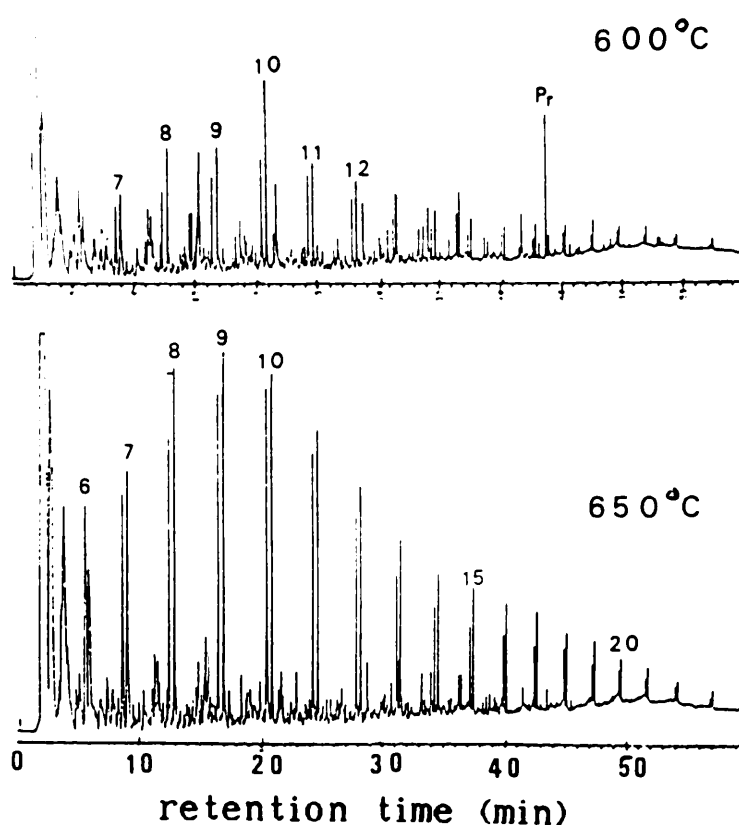


Fig. 2 Pyrograms obtained with Colorado kerogen under helium atmosphere

Numerical and literal indications correspond to those for Fig. 1.

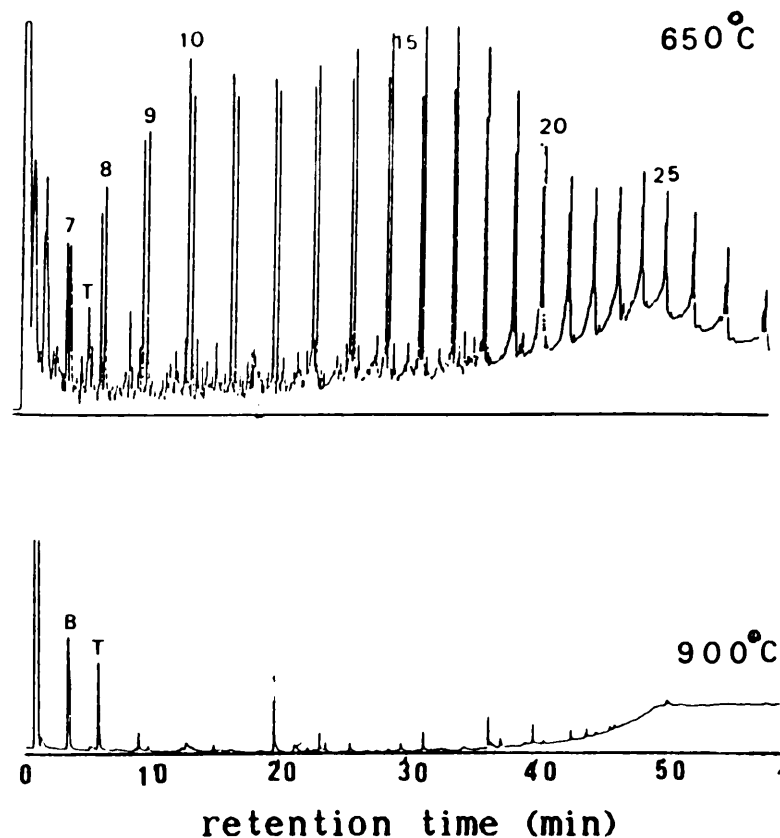


Fig. 3 Pyrograms obtained with Condor oil shale under hydrogen atmosphere

Numerical and literal indications correspond to those for Fig. 1.

series of olefin/paraffin pairs. Successive heating to 800 °C and above results in sharp decrease in the product yield. However, the peaks which represent benzene, toluene and xylene become outstanding. The olefin/paraffin ratio increased with increasing temperature.

Kerogens are similar to respective oil shales in the pyrograms at any temperatures except for the olefin/paraffin ratio. The pyrograms for Colorado kerogen is shown in Fig. 2. It is noted that olefin/paraffin ratio was lower for Colorado kerogen than for Colorado oil shale.

Figure 3 shows the pyrograms obtained with Condor oil shale under hydrogen flow. Comparison of these pyrograms with those obtained under He shown in Fig. 1b leads to the findings that the formation of benzene and toluene at 900 °C was enhanced by H₂ and that the carbon number distribution of olefin/paraffin homologous series was shifted to heavy side.

DISCUSSION

It is generally recognized that kerogen consisted of a complicated polymer core connected with various branch groups consisting of n-alkanes, olefins, naphthenes, isoprenoids, aromatic hydrocarbons and/or hetero-organic compounds by various linkage groups such as methylene, ester and ether²⁾. The core is supposed to be mainly made up of polynuclear naphthenic and aromatic structures. The variation in the composition of pyrolyzates with temperature indicates that kerogen decomposition pattern

Table 2. Possible bond dissociation reactions in kerogen molecule at various pyrolysis temperatures (R = H, CH₃, C₂H₅, etc.)

Temp.	Products	Possible Reaction	BDE of similar bond (kcal/mol) ⁴⁾
low	alkyl-benzenes		$C_3H_7-CH_2-CH_2-C_6H_5$ 69
			 $C_6H_5-CH_2-CH_2-C_6H_5$ 57
	prist-1-ene		$CH_3O-C(CH_3)_3$ 69
	thiophenes		
middle	olefins/paraffins	$\sim CH_2-CH_2-CH_2R$	$C_2H_5-CH_2-CH_2$ 81
		$\sim O-C(=O)-CH_2R$	$CH_3-C(=O)-CH_2$ 79
high	benzene/toluene		$C_6H_5-CH_3$ 99

(under H₂)



changes with temperatures. On the basis of the present data, the carbon skeleton structure of the kerogens are schematically described as follows. (1) Clusters containing isoprenoids, alkyl benzene and thiophene groups may be connected to kerogen cores by weak bonds which dissociate in the early stage of the pyrolysis. (2) Majority of unbranched long chains are connected to the kerogen cores by the bonds with intermediate bond dissociation energies (BDEs). These give the product predominantly consisting of olefin/paraffin homologous series at 650-700 °C. The compounds produced at higher temperatures may be derived from the groups connected to kerogen cores by stronger bonds. These are summarized in Table 2.

Mineral matter may not significantly affect above mentioned fragmentation as kerogens and respective oil shales give similar product pattern.

The presence of H₂ accelerates the formation of benzene and toluene at high temperatures. This may be accounted for by attack of hot H radical on aromatic carbons³⁾. The present results indicate that the product spectra are significantly different, owing to the characteristic structures of kerogens in the shales. The product distribution changed significantly with temperature and the presence of hydrogen, although the small size/high speed pyrolysis possibly gives the results which are different from those in large scale industrial pyrolysis.

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