

PYROLYTIC STUDIES OF ORGANIC COMPONENTS IN ANTARCTIC CARBONACEOUS CHONDRITES Y-74662 AND ALH-77307

Tatsushi MURAE, Akimasa MASUDA and Takeyoshi TAKAHASHI

*Department of Chemistry, Faculty of Science, University of Tokyo,
3-1, Hongo 7-chome, Bunkyo-ku, Tokyo 113*

Abstract: The organic components of two Antarctic carbonaceous chondrites, Y-74662 (C2) and ALH-77307 (C3), have been investigated by pyrolysis using a Curie point pyrolyzer equipped with GC or GC-MS. Although a number of aromatic compounds have been detected as the pyrolysis products of Y-74662 along with a small amount of *n*-alkanes, only a few aromatic compounds in small quantities and no *n*-alkane have been detected in the components produced on the pyrolysis of ALH-77307.

1. Introduction

A great deal of efforts have been made to characterize the organic matter in meteorites and the major part of the recent work has been concerned with non-extractable organic polymer which was considered to be a main component of the organic matter in carbonaceous chondrites (STUDIER *et al.*, 1972; LEVY *et al.*, 1973; BANDURSKI and NAGY, 1976; HAYATSU *et al.*, 1977, 1980; HOLZER and ORÓ, 1979; SMITH and BUSECK, 1981, 1982; YANG and EPSTEIN, 1983) along with amino-acids (*e.g.* CRONIN *et al.*, 1979; SHIMOYAMA *et al.*, 1979). Gas chromatographic examination of the pyrolysis products is one of the effective methods for investigation of organic polymers and the methodology has been applied to the investigation of organic components in meteorites (HAYES and BIEMANN, 1968; STUDIER *et al.*, 1968, 1972; SIMMONDS *et al.*, 1969; LEVY *et al.*, 1973; BANDURSKI and NAGY, 1976; HOLZER and ORÓ, 1979).

In this paper, the authors report the results of pyrolytic studies of organic components in antarctic carbonaceous chondrites Y-74662 and ALH-77307.

2. Sample Preparation and Experimental Apparatus

Samples used in the present work were ALH-77307 (C3) and Y-74662 (C2). The uncrushed whole lump of ALH-77307 was washed with *n*-hexane and crushed into powder, which was extracted with *n*-hexane and then with benzene-methanol (2:1). Both of the powdered samples before and after the extraction were used for pyrolytic investigation. The sample of Y-74662 for pyrolysis was prepared by powdering a piece (*ca.* 300 mg) obtained by rough crushing of the delivered lump of Y-74662 which was washed with *n*-hexane before crushing.

Pyrolyses were carried out using a Curie point pyrolyzer (Japan Analytical Industry Co., LTD: Model JHP-2) at various temperatures. The powdered sample of the meteorite was wrapped with a pyrofoil. The sample in the pyrofoil was preheated at 160°C for 20 min in the stream of carrier gas (nitrogen for GC and helium for GC-MS). The

volatile compounds which might be adsorbed on the surface of the meteorite in the terrestrial environment were exhausted through a valve situated at the connector between the carrier line and the GC capillary column. The carrier line made with the same type capillary column (1.5 m) as that for GC was maintained at 220°C. The temperature of the pyrofoil reached to that for pyrolysis within 0.3 s by applying electrical heating with high frequency. In 1 s after pyrolysis for 3 s the exhaust valve was closed to introduce the products into the analyzing system. Flow rate of carrier gas during analysis (exhaust valve closed) was 0.57 ml/min and then increased to 8.6 ml/min on opening the exhaust valve. The change of the flow rate along with an inserted glass above the pyrofoil in the pyrotube was effective for prevention of the diffusion of the pyrolysis products and for formation of sharp peaks (high resolution) in the chromatogram.

The analyses by GC were carried out using a Shimadzu 7A-PF instrument equipped with an FID for detection. An open tubular fused silica capillary column (25 m × 0.2 mm i.d.) was coated with silicon OV-101. An increasing rate of temperature for GC analysis was programmed to be 4 °C/min from 50 to 220 °C after keeping the initial temperature for 8 min. A JEOL JMS D-300 mass spectrometer equipped with a JMA-2000 mass data analyzer system and the same capillary column as for the GC was used for GC-MS analyses and the column was inserted directly into the ionization chamber of the mass spectrometer.

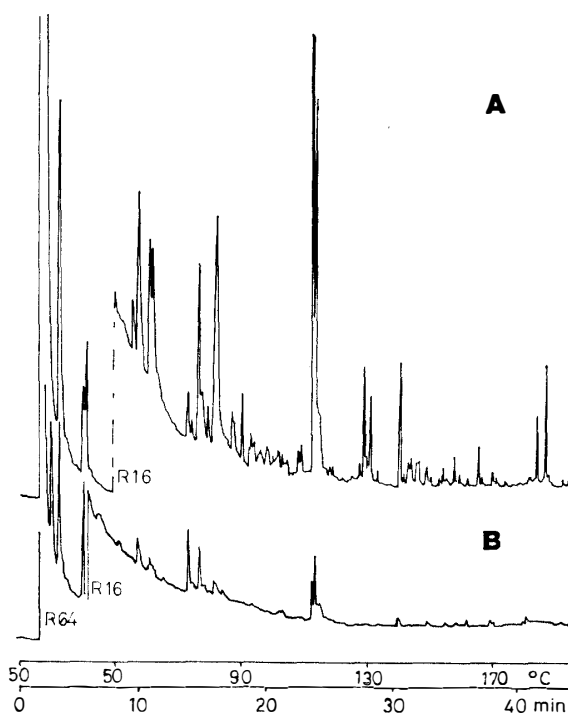


Fig. 1. Gas chromatograms obtained by pyrolysis of 5 mg of Y-74662 (A) (before extraction) and 15 mg of ALH-77307 (B) (after extraction) using 670°C pyrofoil.

3. Results and Discussion

Volatile compounds which were released on heating at 160 °C during preheating were neglected in our experiments in order to obtain clear information on polymeric compound. The current system enabled us to analyze the compounds bearing a higher boiling point than those observed by the conventional pyrolysis-GC (-MS) analyses (e.g. BANDURSKI and NAGY, 1976).

Although minor changes of relative intensity among the peaks were observed, the patterns of chromatogram were essentially the same at different pyrolyzing temperatures. Pyrolyzed components were obtained in a large quantity at the temperature of 670 to 764 °C suggesting that the temperature was most effective for the pyrolysis. This temperature was also most effective for the pyrolysis of ALH-77307. No remarkable change was observed between the chromatograms obtained by the pyrolysis of ALH-77307 before and after the extraction. For the pyrolysis of Y-74662 only the sample before the extraction was used in this work.

Figure 1 shows the gas chromatograms resulting from the pyrolysis of 5 mg of Y-74662 (A) (before extraction) and 15 mg of ALH-77307 (B) (after extraction) using 670 °C pyrofoil. The chromatogram of pyrolysis products of ALH-77307 (Fig. 1B) shows only a few compounds as detectable peaks in spite of the usage of three times

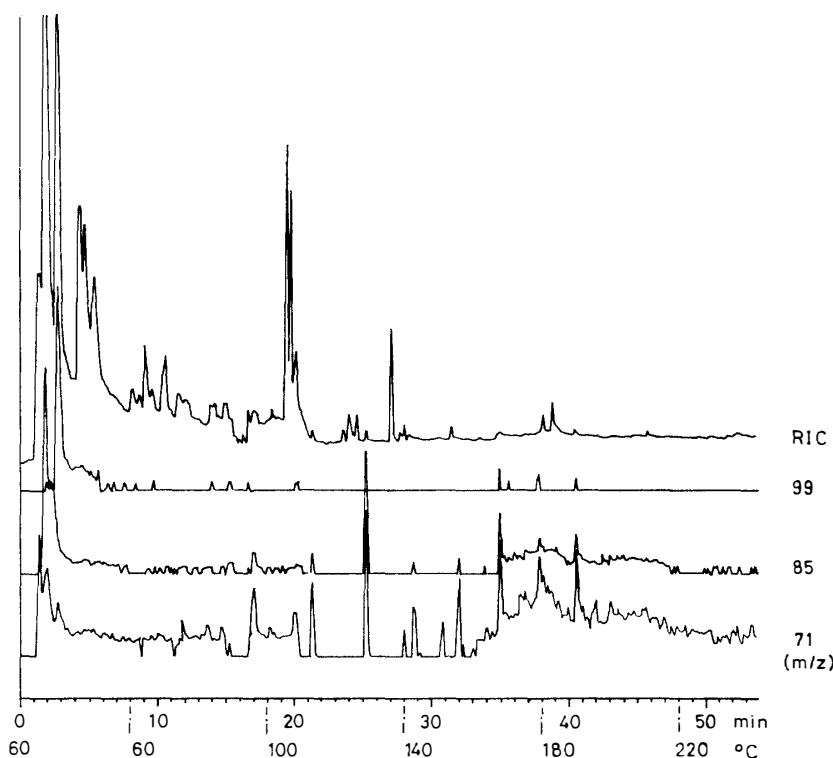
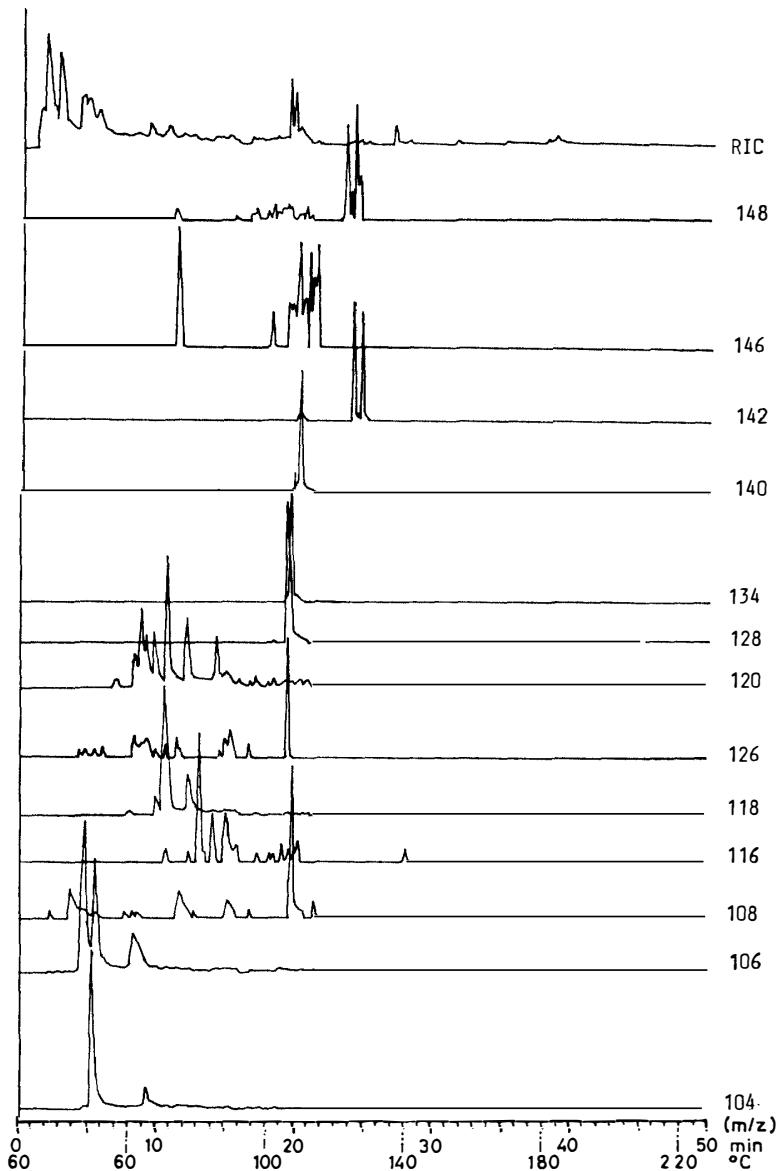


Fig. 2. Survey of *n*-alkanes with mass chromatograms by the ions at m/z 71, 85 and 99 in 10-mg pyrolysis products of Y-74662 (before extraction) using 740°C pyrofoil. RIC: total ions detected in scan range, scan range: m/z 60–360, scan speed: 1.9 s/scan, scan interval: 8.0 s, ionization voltage: 26 V, ion multiplier voltage 1.4 kV. The increasing rate of temperature of GC oven was programmed to be 4°C/min from 60 to 220°C after keeping the initial temperature for 8 min.



Figs. 3(a, b). Mass chromatograms of 10-mg pyrolysis of Y-74662 (before extraction) by the ions listed in Table 1. There is no correlation between the intensities of chromatograms for different mass unit ions. The conditions for the analysis are the same as in Fig. 2.

larger amount of the meteorite sample compared with Y-74662. Although ALH-77307 has been classified into C3, no *n*-alkane was detected in its pyrolysis products by the inspection of the mass spectra obtained by GC-MS. This fact is contrary to the trend in *n*-alkane contents ($C1 < C2 < C3$) pointed out by BANDURSKI and NAGY (1976).

Figure 2 shows the mass chromatographic survey of *n*-alkanes in pyrolysis product (extractable components might be involved in this product) of Y-74662 using the ions at *m/z* 71, 85 and 99. The result suggests that the amount of *n*-alkanes is very small compared with other components. Figures 3(a, b) show the mass chromatograms using the ions which were observed in the mass spectra obtained on the pyrolysis of Y-74662.

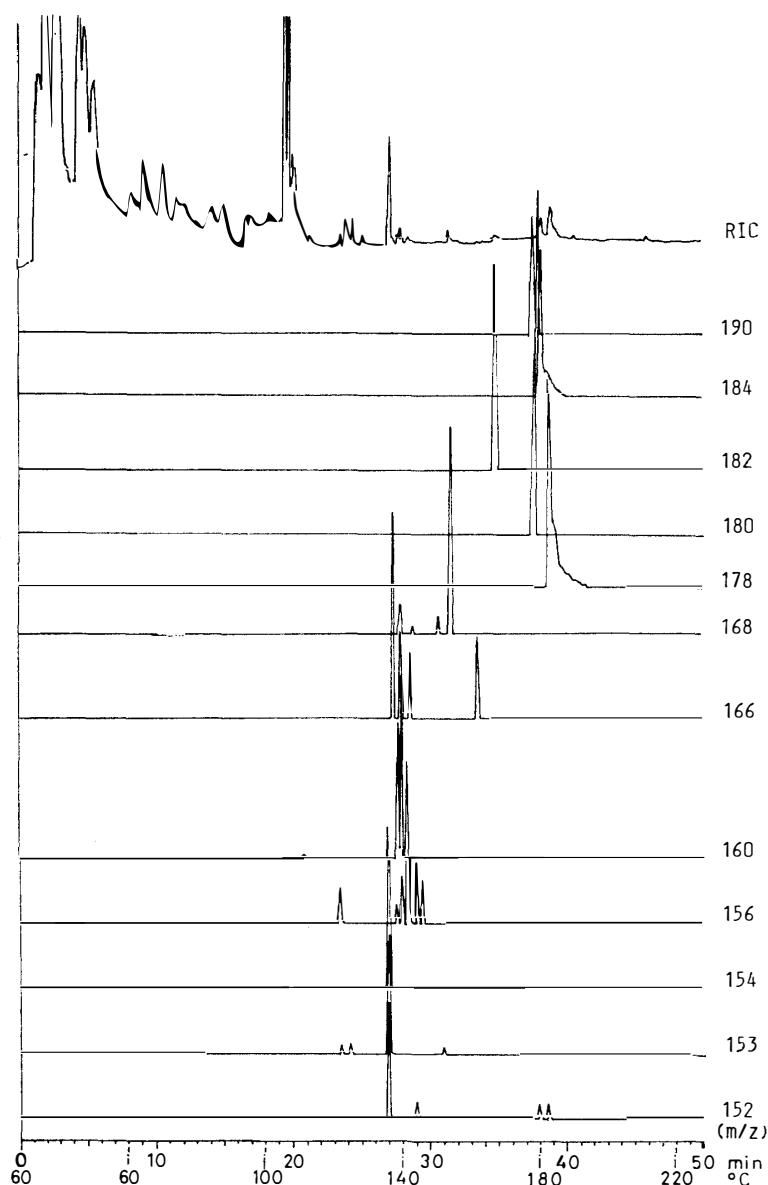

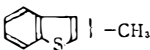
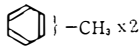


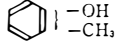
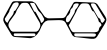

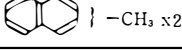
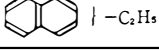

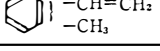
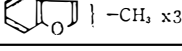
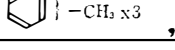


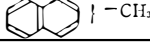
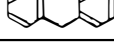
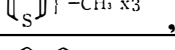




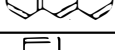
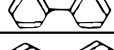
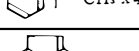


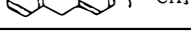

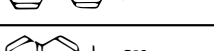

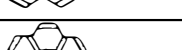
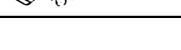



Fig. 3b.

All peaks in GC chromatogram other than *n*-alkanes did not show any remarkable fragmentation except for demethylation in their mass spectrum. This fact suggests that all of these compounds are aromatic. Some of the possible structures (but not all) of the compounds from their molecular ion are listed in Table 1. Many of the compounds which have a higher molecular weight than naphthalene in Table 1 have not been reported in the previous pyrolytic studies on meteorites (ALHA77306,17 and Murchison: HOLZER and ORÓ, 1979; Orgueil: BANDURSKI and NAGY, 1976; Allende: SIMMONDS *et al.*, 1969). The polynuclear aromatic ring systems found in pyrolytic components of Y-74662 are closely related to those (excepting heterocyclic compounds) reported in aromatic acids from oxidation of the Murchison polymer by HAYATSU *et al.* (1977). These polynuclear aromatic compounds seem to reflect a process of graphite

Table 1. Molecular ions detected for the pyrolytic components of Y-74662 and tentative identification of their structures.

| <i>m/z</i> | Tentative Identification | <i>m/z</i> | Tentative Identification |
|------------|---|------------|---|
| 104 |  | 148 |  |
| 106 |  ,  | 152 |  |
| 108 |  | 154 |  |
| 116 |  | 156 |  ,  |
| 118 |  ,  | 160 |  |
| 120 |  ,  ,  | 166 |  or  |
| 126 |  ,  ,  | 168 |  |
| 128 |  | 178 |  or  |
| 134 |  or  | 180 |  or  |
| 140 |  | 182 |  |
| 142 |  | 184 |  |
| 146 |  | 190 |  |

formation from some simple compounds during meteorite formation. And the difference of the pyrolytic components between ALH-77307 and Y-74662 may correspond to the degree of the graphitization of organic matter in these meteorites. It is necessary to confirm the structure of each component without ambiguity for further discussion. Therefore, a careful comparison of authentic samples with the chromatographic peaks given by the pyrolysis is under way because of the difficulty in the structure determination of them by mass spectrum alone.

References

- BANDURSKI, E. L. and NAGY, B. (1976): The polymer-like organic material in the Orgueil meteorite. *Geochim. Cosmochim. Acta*, **40**, 1397-1406.
- CRONIN, J. R., PIZZARELLO, S. and MOORE, C. B. (1979): Amino acids in Antarctic carbonaceous chondrite. *Science*, **206**, 335-337.
- HAYATSU, R., MATSUOKA, S., SCOTT, R. G., STUDIER, M. H. and ANDERS, E. (1977): Origin of organic matter in the early solar system—VII. The organic polymer in carbonaceous chondrites. *Geochim. Cosmochim. Acta*, **41**, 1325-1339.
- HAYATSU, R., WINANS, R. E., SCOTT, R. G., MCBETH, R. L., MOORE, L. P. and STUDIER, M. H. (1980): Phenolic ethers in the organic polymer of the Murchison meteorite. *Science*, **207**, 1202-1204.
- HAYES, J. M. and BIEMANN, K. (1968): High resolution mass spectrometric investigations of the organic constituents of the Murray and Holbrook chondrites. *Geochim. Cosmochim. Acta*, **32**, 239-267.
- HOLZER, G. and ORÓ, J. (1979): The organic composition of the Allan Hills carbonaceous chondrite (77306) as determined by pyrolysis—gas chromatography—mass spectrometry and other meth-

- ods. *J. Mol. Evol.*, **13**, 265–270.
- LEVY, R. L., GRAYSON, M. A. and WOLF, C. J. (1973): The organic analysis of the Murchison meteorite. *Geochim. Cosmochim. Acta*, **37**, 467–483.
- SHIMOYAMA, A., PONNAMPERUMA, C. and YANAI, K. (1979): Amino acids in the Yamato carbonaceous chondrite from Antarctica. *Nature*, **282**, 394–396.
- SIMMONDS, P. G., BAUMAN, A. J., BOLLIN, E. M., GELPI, E. and ORÓ, J. (1969): The unextractable organic fraction of the Pueblito de Allende meteorite; Evidence for its indigenous nature. *Proc. Natl Acad. Sci. U.S.A.*, **64**, 1027–1034.
- SMITH, P. P. K. and BUSECK, P. R. (1981): Graphitic carbon in the Allende meteorite; A microstructural study. *Science*, **212**, 322–324.
- SMITH, P. P. K. and BUSECK, P. R. (1982): Carbyne forms of carbon; Do they exist? *Science*, **216**, 984–986.
- STUDIER, M. H., HAYATSU, R. and ANDERS, E. (1968): Origin of organic matter in early solar system —I. Hydrocarbons. *Geochim. Cosmochim. Acta*, **32**, 151–173.
- STUDIER, M. H., HAYATSU, R. and ANDERS, E. (1972): Origin of organic matter in early solar system —V. Further studies of meteoritic hydrocarbons and a discussion of their origin. *Geochim. Cosmochim. Acta*, **36**, 189–215.
- YANG, J. and EPSTEIN, S. (1983): Interstellar organic matter in meteorites. *Geochim. Cosmochim. Acta*, **47**, 2199–2216.

(Received June 2, 1984; Revised manuscript received July 27, 1984)