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Note

Gas chromatographic analyses of the products obtained on pyrolysis of methane during chemical vapor deposition of carbon

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The pyrolysis of methane has been employed in the preparation of various types of carbonaceous deposits[1,2], and previous studies have shown that a wide variety of species can occur in the gas phase[3–7]. In a limited number of cases, gas chromatography (GC) has been used to examine the pyrolysis products. Such studies have provided information regarding (1) hydrogen and methane[4,5] (2) aliphatic products[6] or (3) aromatic products[7]. Thermodynamic calculations[3] have shown that both aromatic and aliphatic compounds, as well as hydrogen, are major equilibrium products of methane pyrolysis. A model for chemical vapor deposition (CVD) of carbon has been presented[8] which attributes deposition to both acetylenic and aromatic species.

The literature cited indicated that simultaneous analyses of aliphatic and aromatic compounds would provide a more complete description of pyrolysis reactions. This note describes a temperature-programmed GC method suitable for the determination of hydrogen, aliphatic compounds and two aromatic compounds (benzene and toluene). In order to determine the extent of contamination or oxidation during pyrolysis, the method was also designed to separate air, carbon monoxide and carbon dioxide.

EXPERIMENTAL

Chromatograms were obtained by means of a Hewlett-Packard Model 7620 chromatograph utilizing a thermal-conductivity detector connected in series with a Model 3370B digital integrator (Hewlett-Packard) and a Honeywell 193 recorder. The output from the integrator was set in the logarithmic mode so that all peaks could be recorded on scale. The column (12 ft. × 0.125 in. O.D.) was a stainless-steel tube packed with Porapak Q (80–100 mesh). The following conditions were employed: injector temperature, 250°; detector temperature, 300°; detector auxiliary compartment temperature, 300°; bridge current, 150 mA; carrier gas flow-rate (helium; grade A, passed through molecular sieve 5A), 30 ml/min. The oven program was as follows: (1) isothermal for 1 min at −30°; (2) 10°/min to 30°; (3) 30°/min to 200°; (4) isothermal for 1 min at 200°; (5) 30°/min to 270°; (6) isothermal for 8 min at 270°.

Pyrolysis of ultra-high-purity methane (Matheson, Coleman & Bell, East Rutherford, N.J., U.S.A.) was performed in static and flow systems at 1050–1460°.

Gas samples were removed by means of a Precision Sampling Series A-2 gas-tight syringe. The syringe was filled at reduced or atmospheric pressure, the syringe valve closed and the gas compressed to 0.3 or 0.5 ml. Compression of the gas in the syringe was performed to prevent leakage of air into the sample. Immediately prior to injection, the syringe valve was opened to insure that the selected volume was delivered at local atmospheric pressure (625 torr).

RESULTS AND DISCUSSION

A series of chromatograms obtained as pyrolysis of methane proceeded in the static system are shown in Fig. 1 and one obtained from the flow system is shown in Fig. 2. They allow identification of the pyrolysis products hydrogen, methane, acetylene, ethylene, ethane, propene, propane, C_4 hydrocarbons, C_5 hydrocarbons, benzene and toluene, as well as the contaminants nitrogen, oxygen, carbon monoxide, carbon dioxide and water. Separation of the latter group does not require at least two columns,

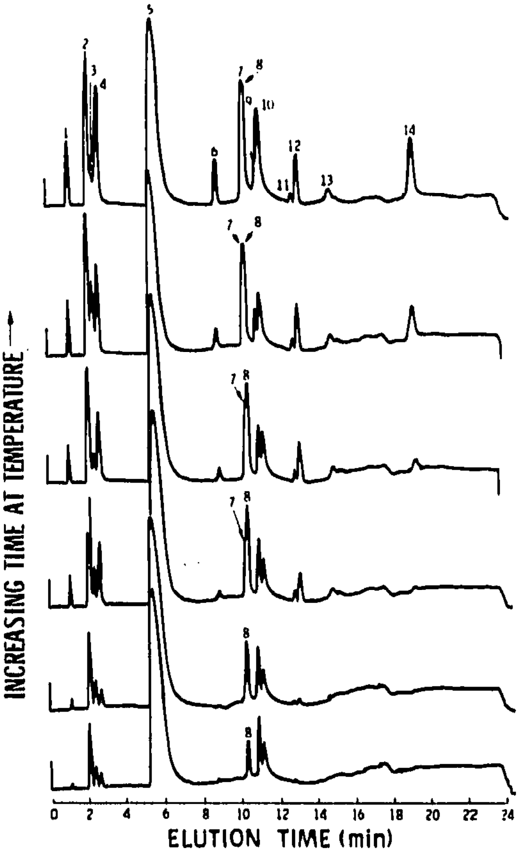

Fig. 1. Chromatograms obtained from a static system during the pyrolysis of methane. Carrier gas (helium) flow-rate, 30 ml/min. Sample size, 0.3 ml. 1 = Hydrogen; 2 = nitrogen; 3 = oxygen; 4 = carbon monoxide; 5 = methane; 6 = carbon dioxide; 7 = acetylene; 8 = ethylene; 9 = ethane; 10 = water; 11 = propene; 12 = propane; 13 = C_4 hydrocarbon; 14 = benzene.

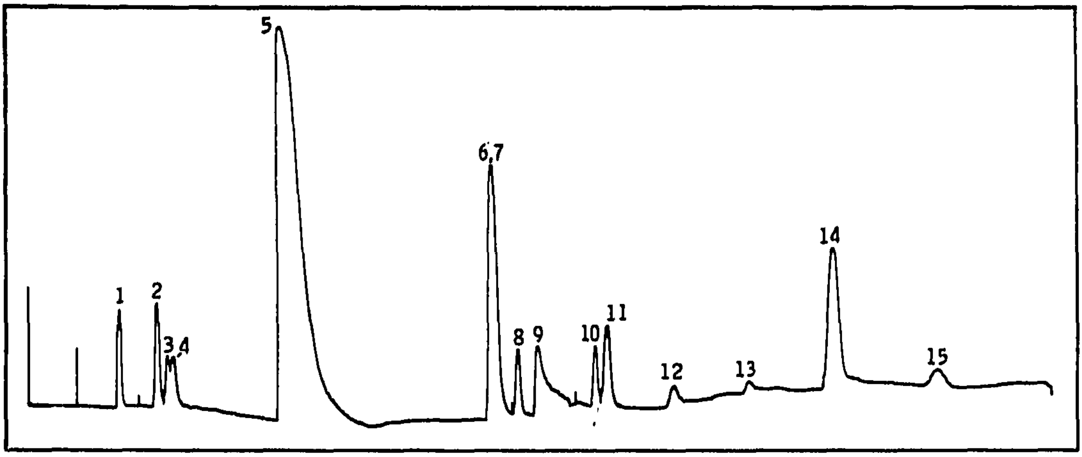

Fig. 2. Chromatogram obtained from a flow system during the pyrolysis of methane. Carrier gas (helium) flow-rate, 33 ml/min. Sample size, 0.5 ml. 1 = Hydrogen; 2 = nitrogen (1036); 3 = oxygen (384); 4 = argon (372); 5 = methane (3379 × 10^2); 6 = acetylene and 7 = ethylene (1412 × 10^1); 8 = ethane (580); 9 = water (1703); 10 = propene (532); 11 = propane (836); 12 = C_4 hydrocarbon; 13 = C_5 hydrocarbon; 14 = benzene (5650); 15 = toluene. Representative uncorrected peak areas (μV·sec) are given in parentheses. Note the reversal of the hydrogen peak.

as has been stated elsewhere[9]. Fig. 2 shows that argon (introduced prior to the start of pyrolysis) can be separated from nitrogen and oxygen. If the initial oven temperature is decreased from −30 to −70°, argon can also be separated from carbon monoxide. Relative retention times are given in Table I.

The chromatographic method described had two drawbacks: (1) quantitative data for hydrogen could not be obtained for all the chromatograms because of the well known[9,10] peak-reversal characteristics of this gas in helium as carrier gas (see Fig. 2, for example); (2) separation of acetylene and ethylene was insufficient to yield

TABLE I

GC RETENTION TIMES RELATIVE TO HYDROGEN

Species	*Retention time (min)*	*S.D. (min)*	*Number of points**
Nitrogen	1.033	0.015	6
Oxygen	1.313	0.019	6
Carbon monoxide	1.590	0.022	6
Methane	4.352	0.040	6
Carbon dioxide	7.808	0.042	6
Acetylene	9.185	0.007	2
Ethylene	9.328	0.051	5
Ethane	9.923	0.051	6
Water	10.112	0.066	6
Propene	11.840	0.059	5
Propane	12.114	0.059	5
C_4 hydrocarbons	13.840	0.075	4
Benzene	18.198	0.085	4

* Data taken exclusively from the chromatograms in Fig. 1.

quantitative results for either of the species. Indeed, even the qualitative identification of both species was sometimes difficult; other, presumably identical, columns failed to show any separation of acetylene and ethylene, as in Fig. 2. However, the technique allowed simultaneous determination of aliphatic and contaminant species as well as two aromatic compounds, and enabled qualitative description of the gas-phase reactions which occur during CVD of carbon from methane.

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REFERENCES

1 H. B. Palmer and C. F. Cullis, in P. L. Walker, Jr. (Editor), *Chemistry and Physics of Carbon*, Vol. 1, Marcel Dekker, New York, 1966, pp. 265–325.
2 J. C. Bokros, in P. L. Walker, Jr. (Editor), *Chemistry and Physics of Carbon*, Vol. 5, Marcel Dekker, New York, 1969, pp. 1–118.
3 R. E. Duff and S. H. Bauer, *Los Alamos Rept. LA-2556*, September 1961.
4 J. D. Brooks, W. R. Hesp and D. Rigley, *Carbon*, 7 (1969) 261.
5 J. P. Blakely and L. G. Overholser, *Carbon*, 5 (1967) 87.
6 S. D. Robertson, *Carbon*, 10 (1972) 221.
7 J. Oró and J. Han, *Science*, 153 (1966) 1393.
8 M. L. Lieberman, in F. A. Glaski (Editor), *Proceedings of the Third International Conference on Chemical Vapor Deposition*, American Nuclear Society, 1972.
9 P. K. Basu, C. J. King and S. Lynn, *J. Chromatogr. Sci.*, 10 (1972) 479.
10 J. E. Purcell and L. S. Ettre, *J. Gas Chromatogr.*, 3 (1965) 69.