April, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***66****, 1265—1268(1993)* 1265

Studies on Identification of Soot. V. Changes in Alkylbenzenes and Alkanes in Diffusion Flame

Masahisa TAKATSU* and Tadahiro YAMAMOTO†
Forensic Science Laboratory, Hyogo Prefectural Police Headquarters, Shimoyamate-dori, Chuo-ku, Kobe 650
†Department of Applied Chemistry, Himeji Institute of Technology, Shosha, Himeji 671-22

(Received April 9, 1992)

Changes in the diffusion flames of benzene, toluene, *p*-xylene, ethylbenzene, styrene, cumene, octane, and decane fuels were comparatively examined. Original fuels and dealkylation products were observed in the flames of the alkylbenzenes. Styrene was also found as an elimination product in the flames of ethylbenzene and cumene. The profiles of these products should depend on the structures of the side chains of the original alkylbenzenes. On the other hand, the two alkanes were easy to cleave and changed into smaller alkenes in the flame faster than the six other alkylbenzenes.

Many studies of flames have been published in order to determine the mechanism of soot generation. The fuels used in those studies were both aliphatic and aromatic hydrocarbons which included methane,[1—3] ethene,[4] ethyne,[4—8] propane,[9] hexane,[10] heptane,[11] kerosene,[12] light oil,[13] benzene,[7,9,12,14,15] and toluene.[15] However, those studies do not include a comparative evaluation among the various fuels, and the fuels were often burned in air diluted with an inert gas,[14] at low pressure,[4—7,9,13] or in a shock tube.[15]

We have been studying the discrimination of several kinds of soot to investigate the cause of accidental fires. When fuels have been completely burned, the remaining soot at the scene of the accident may be invaluable evidence for the determination of the fuel. Since an accidental fire usually happens in the atmosphere, we have collected comparative burning data obtained under normal atmospheric conditions. In our previous studies[16,17] of the pyrolysis of soot, the determination of aromatic hydrocarbons used as a fuel was possible in some cases by detecting the original fuels, dealkylation products, elimination products, etc. in the soot. In this paper, changes in the original fuels in the diffusion flames were examined by means of analyzing the flame gas for alkylbenzenes and alkanes by gas chromatography.

Experimental

Fuels. Benzene, toluene, *p*-xylene, ethylbenzene, styrene, cumene, octane, and decane used as fuels were obtained from Wako Pure Chemical Industries, Ltd. as special grade reagents. The purities of these fuels were found to be sufficient, and the fuels were used without further purification.

Collection of Flame Gas. Gas samples were collected from the diffusion flames of both alkylbenzenes and alkanes. The liquid fuel from a glass container (2 cm diameter, 6 cm height) was supplied to the upper part of a cotton core by capillary action, and was then burned in the atmosphere. Each flame was controlled to a constant 4 cm height. After the flame became stable, gas samples from each flame were collected at five positions (0—4), which signify height (*H*/cm) from the top of the cotton core as shown in Fig. 1, along the axis of the flame using a gas-tight syringe wrapped with aluminium foil. Fuel burning rates were about 0.5 ml min^{-1}.

Apparatus and Analysis Conditions. A Shimadzu 6A gas Chromatograph equipped with a flame ionization detector and a 3m×3mm i.d. glass column with 20% SE-30 on 60/80 mesh Chromosorb W(AW), and a Shimadzu CR-6A chromatogram processor were used. After injection of the gas sample, the column oven temperature was programmed from 80 to 230°C at a rate of 10°C min^{-1} as used in our previous studies.[16,17] Identification of the chromatographic peaks was achieved by comparing the retention times and the mass spectra with those of the authentic compounds. A Shimadzu 7000 gas chromatograph/mass spectrometer was used for the mass spectrometric analysis.

Results and Discussion

Diffusion Flame of Alkylbenzenes. Two examples of the obtained gas chromatograms are shown in Fig. 2. In alkylbenzene flames, C2 compounds (including ethyne), benzene, toluene, styrene, and the fuels were detected as stable compounds. Mole fractions of these stable hydrocarbons were calculated and are plotted in Fig. 3. In the lowest position, the original alkylbenzenes were predominantly observed. In the

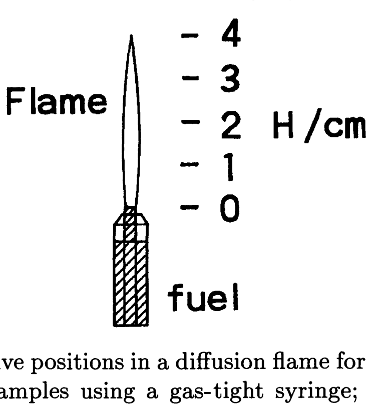


Fig. 1. Five positions in a diffusion flame for collection of gas samples using a gas-tight syringe; the flame height is about 4 cm, and the five positions are represented as distances (*H*/cm) from the top of a cotton core.

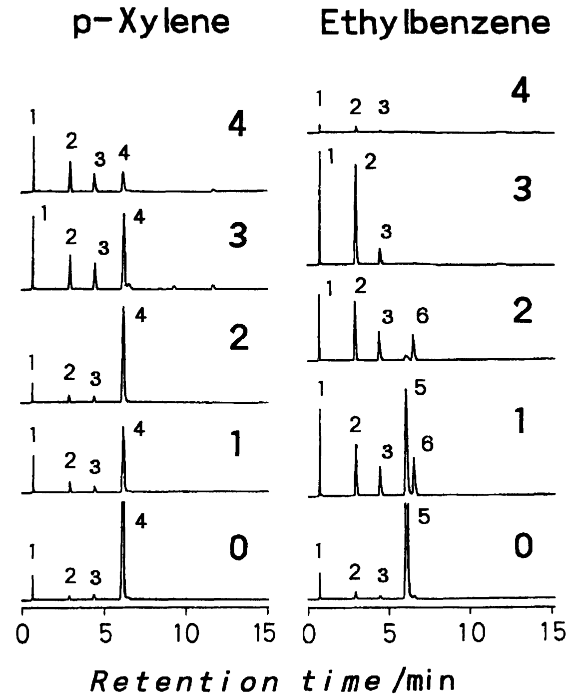
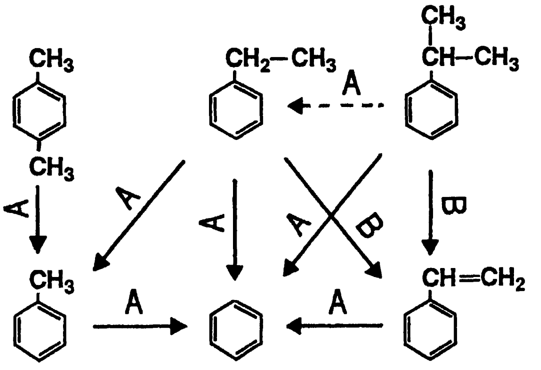


Fig. 2. Gas chromatograms of gas samples collected at the five positions in the diffusion flame of *p*-xylene and ethylbenzene. 1: C2 compounds, 2: Benzene, 3: Toluene, 4:*p*-Xylene, 5: Ethylbenzene, 6: Styrene.



Scheme 1. Possible changes in the alkylbenzenes by dealkylation (A) and elimination (B) in the flame; a change to a minor product is shown by a dotted line.

flames of benzene, toluene *p*-xylene, and styrene, these fuels could be observed even in the upper position of the flame. The mole fractions of both ethylbenzene and cumene decreased more rapidly than those of the other four fuels.

Benzene was found in the flames of toluene, *p*-xylene, ethylbenzene, styrene, and cumene. Benzene should be produced by the demethylation of *p*-xylene, the deethylation of ethylbenzene, the deethenylation of styrene, and the depropylation of cumene as shown in Scheme 1 as well as being produced from toluene in the shock tube experiment.[15] Toluene was found in the flames of *p*-xylene and ethylbenzene. Toluene should also be produced by the demethylation of *p*-xylene and ethylbenzene as shown in Scheme 1. The absence of toluene in the styrene flame suggests that toluene was difficult to produce from styrene, because its occurrence should require a cleavage of the C=C double bond. Small amounts of toluene and ethylbenzene were found as minor products in the cumene flame.

These compounds were believed to be dealkylation products produced during the pyrolytic cleavage of C–C single bonds, and almost all of them increased in the upper portion of the flame. Styrene found in the flames of ethylbenzene and cumene should be produced by the elimination of a hydrogen molecule and methane, respectively. Occurrence of the elimination in both flames can be confirmed by the formation of many alkenes in the flames of octane and decane, as described in a later section. Styrene could be observed even in the upper portion of the flame. Ethylbenzene and cumene should be less stable than styrene in the flame since their side chains have C–C single bonds which are easy to cleave.

The mole fraction profiles of these stable compounds found in the middle portion of the flames were considerably different from one another among the six alkylbenzenes. These profiles were also in good agreement with those observed during the pyrolysis of soot in our previous studies.[16,17] From this result, it could be conceivable that the products of the benzene and alkylbenzene pyrolysis observed in the soots should be those in the flames.

Changes in the alkylbenzenes in these flames could be assumed as shown in Scheme 1. This flow chart suggests two types of pyrolytic reactions, dealkylation (A) and elimination (B). The occurrence of these reactions seems to depend on the structures of the side chains. First, the C–C single bond tends to cleave easier than the C=C double bond, so that benzene was produced more easily than toluene from styrene. Second, the C–C single bond in the ethyl group tends to change into a C=C double bond with the elimination of a hydrogen molecule or alkane such as methane so that styrene was produced from both ethylbenzene and cumene. Toluene and ethylbenzene produced in the combustion process could also be explained by considering demethylation as shown in Scheme 1.

In the ethylbenzene flame, elimination of a hydrogen molecule and demethylation should occur almost equally since toluene and styrene were observed almost equally. In the cumene flame, however, elimination of methane should occur more predominantly than demethylation since styrene and benzene (which is the deethenylation product of styrene) were mainly observed with only a trace of ethylbenzene and toluene which is the demethylation product of ethylbenzene.

Diffusion Flame of Alkanes. The principal stable compounds observed in the flames of octane and decane were C2 compounds (including ethene), propene, and

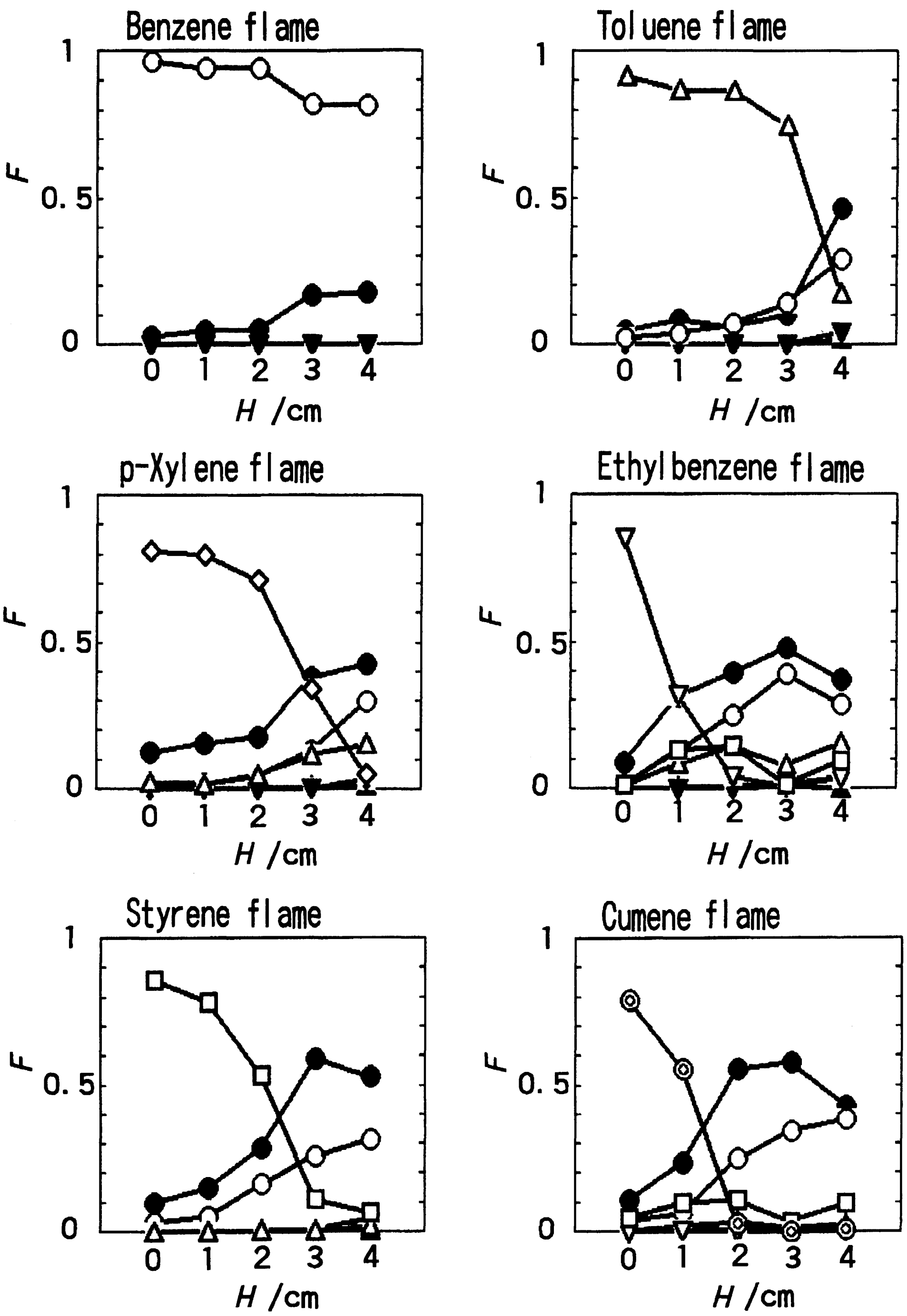


Fig. 3. Mole fraction profiles of stable hydrocarbons in the six alkylbenzene flames. H: Axial distance from the top of the cotton core, F: Mole fraction. ●: C2 compounds, ▲: Propene, ▼: Butene and 1,3-Butadiene, ○: Benzene, △: Toluene, ◇:*p*-Xylene, ▽: Ethylbenzene, □: Styrene, ◎: Cumene.

butene (1-butene and/or 2-butene). These alkenes were observed even in the lowest position of both flames. In the octane flame, 1,3-butadiene, 1-pentene, 1-hexene, and 1,5-hexadien-3-yne (or benzene) were identified as minor compounds. In addition to these products, 1-heptene and 1-octene were also identified as minor products in the decane flame. These 1-alkenes could be identified from their characteristic mass fragmentation patterns. For example, the ions at $m/z = 42$ and 70 in the mass spectrum of 1-heptene were considerably stronger than those of the 2- and 3-heptenes. Mole fraction profiles of the observed stable hydrocarbons are given in Fig. 4. The mole fractions of octane and decane decreased more rapidly than almost all the alkylbenzenes in Fig. 3, and the mole fraction of the C2 compounds increased more rapidly than that in Fig. 3. The alkenes observed should be elimination products produced in the flame. Since many alkenes were also produced from heptane in the

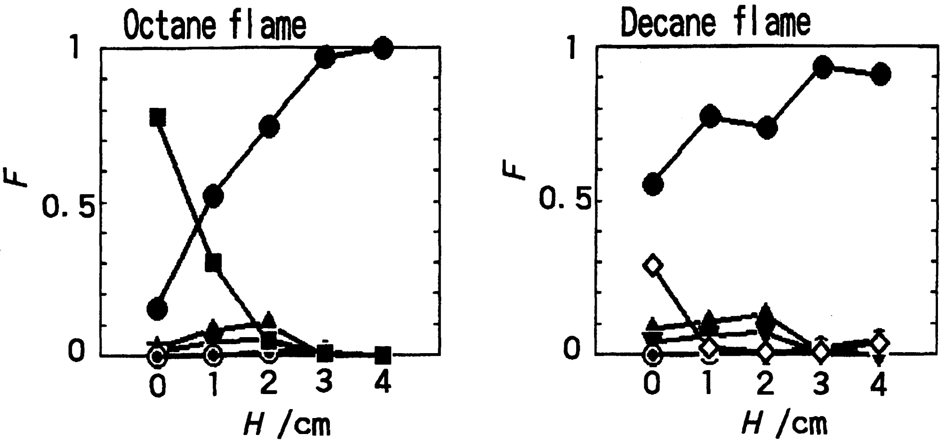


Fig. 4. Mole fraction profiles of stable hydrocarbons in the flames of octane and decane. H: Axial distance from the top of the cotton core, F: Mole fraction. ●: C2 compounds, ▲: Propene, ▼: Butene and 1,3-Butadiene, ◉: 1,5-Hexadien-3-yne (or Benzene), ■: Octane, ◆: Decane.

flame,[11] it is assured that cleavage occurred at every C–C bond.

The profiles of the original fuels, the dealkylation products, and the elimination products observed were in good agreement with those from soot pyrolysis. This suggests that alkylbenzene soots contain these pyrolytic products which are formed in the diffusion flame. Rapid decreases in alkanes in the flame suggest a difficulty in detection of alkanes in the soots,

References

1) G. Prado, A. Garo, A. Ko, and A. Sarofim, *20th. Symp. (International) Combust.*, **1984**, 989.

2) K. C. Smyth, J. H. Miller, R. C. Dorfman, W. G. Mallard, and R. J. Santoro, *Combust. Flame*, **62**, 157 (1985).

3) K. Saito, F. A. Williams, and A. S. Gordon, *J. Heat Transfer*, **108**, 640 (1986).

4) B. D. Crittenden and R. Long, *Combust. Flame*, **20**, 359 (1973).

5) B. L. Wersborg, A. C. Yeung, and J. B. Howard, *15th Symp. (International) Combust.*, **1975**, 1439.

6) J. L. Delfau, P. Michaud, and A. Barassin, *Combust. Sci. Technol.*, **20**, 165 (1979).

7) D. B. Olson and H. F. Calcote, *18th Symp. (International) Combust.*, **1981**, 453.

8) J. L. Delfau and C. Vovelle, *Combust. Sci. Technology*, **41**, 1 (1984).

9) H. Bockhorn, F. Fetting, and H. W. Wenz, *Ber. Bunsen-Ges. Phys. Chem.*, **87**, 1067 (1983).

10) V. G. Spengler and J. Kern, *Brennstoff-Chem.*, **Bd50**, 321 (1969).

11) J. H. Kent and F. A. Williams, *15th Symp. (International) Combust.*, **1975**, 315.

12) G. P. Prado, M. L. Lee, R. A. Hites, D. P. Hoult, and J. B. Howard, *16th Symp. (International) Combust.*, **1977**, 649.

13) A. Clajolo, R. Barbella, M. Mattiello, and A. Dalessio, *19th Symp. (International) Combust.*, **1983**, 1369.

14) J. D. Bittner and J. B. Howard, *18th Symp. (International) Combust.*, **1981**, 1105.

15) J. F. Merklin and C. M. Sorensen, "Final Report for Period February 16, 1984—February 15, 1988," DOE/ER/10677-8, (1988).

16) M. Takatsu and T. Yamamoto, *Nippon Kagaku Kaishi*, **1988**, 1749.

17) M. Takatsu and T. Yamamoto, *Nippon Kagaku Kaishi*, **1991**, 235.