A Mass Spectrometric Investigation of Petroleum. III.[1] The Determination of the Alkyl Side Chain Number on Aromatics in the High Boiling Range Fraction of Petroleum

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Hitherto, the alkyl side chain number on alkyl aromatics in the high boiling range fraction of petroleum has been determined by the infrared spectrometric assigment of the ratios of CH_2 and CH_3. However, the accuracy of this method is not satisfactory, and only a mean value is obtained when there are more than two types of co-existing compounds.

The present author has reported the total carbon number of the alkyl side chain as one of a series of studies of the petroleum fraction.[1,2] In this series of studies, the alkyl side chain number must be determined in order to ascertain the carbon number of each alkyl side chain.

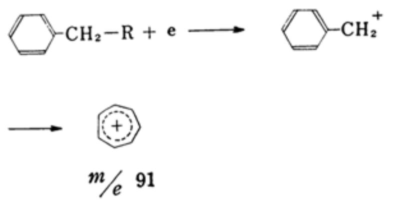
For this purpose, the cleavage mechanism of alkyl aromatics under electron impact was studied, and a method was devised by which the alkyl side chain number could be determined from the finding of the α and β cleavage characteristic of the aromatic ring. Thus mass spectrometry can determine the alkyl side chain numbers for different types of coexisting compounds.

Experimental

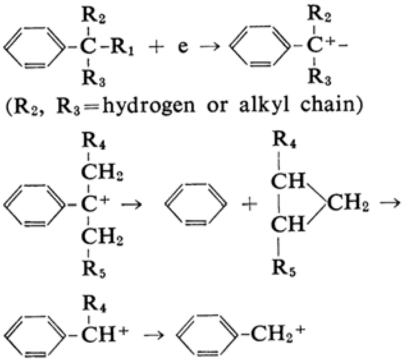
Several authentic aromatics were measured by a Hitachi-RMU 5B type mass spectrometer. Mass spectral data of other unavailable compounds were obtained from the literature.[3]

Theoretical

The Mass Spectra of Alkylbenzene.—Under electron impact n-alkylbenzene is stabilized as the tropylium ion according to the β bond cleavage.[4] Therefore, m/e 91 is a very intense peak in the spectrum.



However, branched alkylbenzene at the α-position cleaves itself to yield the m/e $(89+R_2+R_3)$ ion, and some of these ions decompose into the m/e $(91+R_4)$ or the m/e $(91+R_5)$ ion, the m/e 91 ion are produced by further rearrangement.[5-7]



(R_2, R_3=hydrogen or alkyl chain)

Alkylbenzene with more than two alkyl substituents takes an α cleavage in addition to the β cleavage described above. When the substituent is longer than the propyl group, the cleavage of the β bond is observed, while the α cleavage is observed when it is the methyl or ethyl group.

Thus, monosubstituted alkylbenzenes give their most intense peak according to the β cleavage, while polysubstituted alkylbenzenes give intense peaks according to the β and α cleavages as well.

The following equation indicates the carbon number of the alkyl side chain on the ion produced according to the β cleavage:

$$b=a(n-1)/n+1 \qquad (1)$$

where

b: the total carbon number of the alkyl side chain on the ion produced;

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[1] Part II. S. Oshima, A. Katsumata and K. Fujii, *Mass Spectroscopy*, **11**, 46 (1963).

[2] S. Oshima, T. Nishishita and K. Fujii, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 646 (1963).

[3] Catalog of Mass Spectral Data, A. P. I. Research Project 44.

[4] S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

[5] W. H. McFadden and A. L. Wahrhaftig, *J. Am. Chem. Soc.*, **78**, 1572 (1956).

[6] P. N. Rylander and S. Meyerson, ibid., **78**, 5799 (1956).

[7] F. W. McLafferty, *Appl. Spectroscopy*, **11**, 148 (1957).

a: the total carbon number of the alkyl side chain on the original molecule, and

n: the alkyl side chain number.

If the ion is formed according to the α cleavage, on the other hand, the equation will be;

$$b=a(n-1)/n \qquad (2)$$

Since the total carbon number of the alkyl side chain on the ion (b) is obtained from the most intense peak in the spectrum, the alkyl side chain number (n) can be obtained by determining the a value from the most intense peak in the spectrum.

The alkyl side chain number (n) was calculated from Eqs. 1 and 2 for 89 kinds of mass spectral data of authentic alkylbenzenes possessing from 3 to 12 carbons in the alkyl side chain and involving from 1 to 6 alkyl side chain numbers. Figure 1 indicates the relationship between the real side chain number and n from Eqs. 1 and 2. The n values which were derived from the β cleavage process agree with the real value when the chain number is small, but they differ when the chain number becomes more than three. On the other hand, the n from the α cleavage process shows good agreement with the real value when the chain number is large, but they differ greatly when the chain number is less than 4.

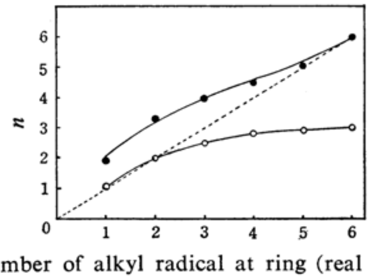


Fig. 1. Number of alkyl radical at ring (real value) and n at alkylbenzene.
● α-cleavage ○ β-cleavage

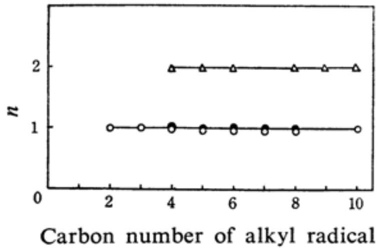
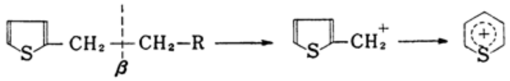


Fig. 2. Carbon number of alkyl radical and n at alkylthiophene.
○ n-alkylthiophene
● iso-(2)-alkylthiophene
△ di-n-alkylthiophene

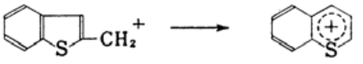
Alkylthiophene.—The most intense peak in the spectrum of alkylthiophene is generally due to the β cleavage of the alkyl side chain. This results from the hypothetical formation of the thiacyclohexatrienium ion, which is similar to the tropylium ion observed in alkylbenzene.

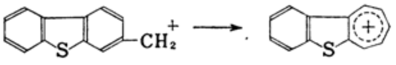


The n values calculated from Eq. 1 for 27 authentic alkylthiophenes showed good agreement with the real values. Figure 2 indicates the relationship between n and the carbon number of the alkyl side chain.

Miscellaneous Compounds.—The most intense peaks in the mass spectra of naphthalene, benzothiophene and dibenzothiophene also result from the β cleavage of alkyl side chains.

These ions are thought to be stabilized by the following process:





The Determination of *a*.—The a value of the high boiling range aromatic fraction in petroleum is determined by the following procedure. An aromatic mixture of petroleum is separated into small fractions by liquid chromatography in order to separate the coexisting compound types which overlap on the same mass numbers in the case of the low voltage ionization method. However, if the mass difference between the two aromatic rings is larger than b, overlapping compound types are permitted to coexist in the same fraction. When these isolated aromatic mixture are measured by the low voltage ionization method, the alkyl carbon number of the most abundant molecule is obtained according to the author's method.[2] Thus, the a value is determined.

The Determination of *b*.—When the isolated sample mentioned above is then measured under 50∼100 eV. to obtain fragment ions, the most intense peak in the spectrum is b. On the other hand, in the presence of more than two types of compounds, the most intense peak among the objective compounds has to be taken as *b*.

The Determination of *n*. — There are two procedures for determining *n* for alkylbenzenes. The first method is to multiply a correction value by *n* as calculated from Eq. 1, assuming β cleavage. Table I indicates the correction value. The other method is as follows; Eq. 1 is used where $n=1$ or 2, Eq. 2 is used where $n=5$ or 6, and the mean value between Eqs. 1 and 2 is used where $n=3$ or 4. Equation 1 is used for alkylthiophene, and it is also adopted for naphthalene, benzothiophene and dibenzothiophene in spite of the scarce calibration data about them.

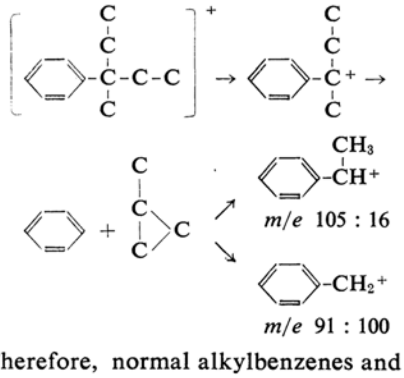
TABLE I. CORRECTION VALUES OF *n*

Chain number	1	2	3	4	5	6
Correction value	1	1	1.2	1.4	1.7	2.0

Discussion

If the most intense fragment peak in the spectrum is a factor determining the alkyl side chain number, the cleavage mechanism should not be influenced by the alkyl side chain number or by other structure requirements.

Monoalkylbenzenes should give the most intense peak on the same mass number. If α carbon has no side chain, monoalkylbenzenes actually give the most intense peak at *m/e* 91 without exception. Methylated (α) monoalkylbenzenes give the most intense peak at *m/e* 105 according to the β cleavage, and the ratio of *m/e* 105 to *m/e* 91 is about 10%. This value is unchanged even if the chain length is changed. Moreover, α-dimethyl monoalkylbenzenes give the most intense peak at *m/e* 119 and the ratio of *m/e* 119 to *m/e* 91 is about 40∼60%, which is also independent of the length of the alkyl side chain. However, when ethyl or a longer alkyl group ($>C_3$) is attached to the α carbon, *m/e* 91 becomes a intense peak. For example, 3-ethyl-3-pentylbenzene is cleaved as follows:



Therefore, normal alkylbenzenes and branched alkylbenzenes having ethyl or a longer alkyl group ($>C_3$) on α carbon are cleaved to form the most intense peak at the same mass number. However, α-methyl monoalkylbenzenes cause an error, as is indicated in Fig. 3. Polysubstituted methyl or ethyl benzene produces α-cleavage rather than β-cleavage ions. Figure 4 shows the ratio of the α cleavage to the β cleavage in the case of dialkylbenzene. When the carbon number of the alkyl chain is C_1 or C_2, a large amount of α cleavage is observed; it would be expected that this inclination would become more marked as the benzene ring is substituted more. This means that an increase in the alkyl side chain number disturbs the determination of the alkyl side chain number from the β-cleaved ion. Accordingly, a correction value is required.

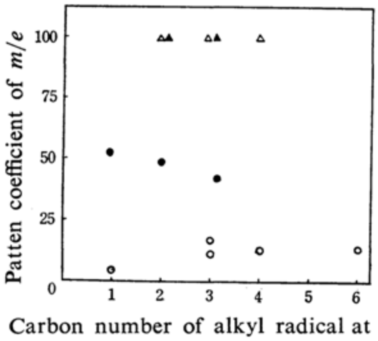
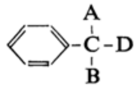


Fig. 3. Peak intensity of *m/e* 91 at monoalkylbenzene.



○ A=CH_3, B=H, ● A=CH_3, B=CH_3
△ A≥C_2H_5, B=H, ▲ A≥C_2H_5, B≥CH_3

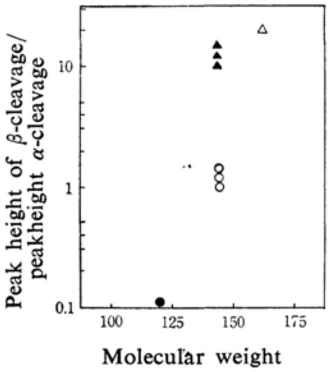


Fig. 4. Ratio of α-cleavage ion to β-cleavage ion at alkylbenzene.
● methylethylbenzene
○ diethylbenzene
▲ methylpropylbenzene
△ dipropylbenzene

Figure 5 shows the effect of the carbon number of the alkyl chain. The n value from the α cleavage tends to decrease as the carbon number increases in n-alkylbenzene. Other alkylbenzenes, however, do not show this inclination. Therefore, the effect of the carbon number should not be considered excessive.

The following facts have been established about the sensitivity of β-cleaved ions. Monoalkylbenzenes are cleaved to form the hydrogen-rearranged m/e 92 ion as well as the m/e 91 ion, and there is a certain relationship between the molecular ion peak height and the summed peak height of m/e 91 and 92. The ratio of the molecular ion and the summed peak height (m/e 91+92) tends to decrease when the number of carbon which are lost as a neutral radical after β cleavage increases. On the other hand, when the number of carbons is within C_3 to C_5, this ratio becames constant.[8] This means that the number of β-cleaved ions is about the same within a certain size range of the alkyl chain. This makes it desirable to use the β cleavage process for the determination of the alkyl side chain number.

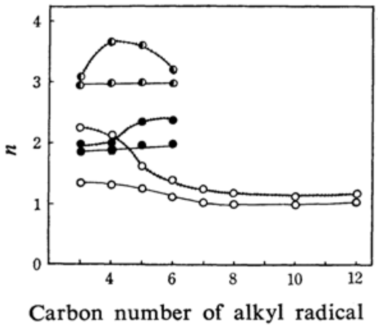


Fig. 5. Carbon number of alkyl radical and n at alkylbenzene.
○ radical number : 1
● radical number : 2
◐ radical number : 3
⧻ α-cleavage — β-cleavage

According to Fig. 1, the choice of Eq. 2 for the determination of the alkyl side chain number is preferable to the C_5 and C_6 of the side chain. However, considering the cleavage mechanism, the chance of error elsewhere is increased.

Alkylbenzenes in the high-boiling-range petroleum fraction are considered to include all kinds of alkylbenzenes. Because of the above reason, the calculated alkyl side chain number is, after all, the average value. Charlet reported that in almost all cases the alkyl side chain number is about 3 to 4 in the high boiling fraction of petroleum.[9] Alkyl side chain numbers (n) calculated from Eq. 1 and corrected according to Table I for alkylbenzene and naphthalene in the aromatic fraction isolated from light gas oil were 3 or 4, which agreed well with the findings of infrared spectrometry. It was clear that a and b could be determined by examining the same sample for which the n was determined.

According to a number of spectral data, it may be considered that the alkyl side chain number of alkylthiophene can be determined by Eq. 1, but much more data are required for naphthalenes, benzothiophenes, dibenzothiophenes and other aromatics.

Summary

The cleavage mechanism of alkylbenzene and other compounds under electron impact has been studied. The following facts are evident. If the ion from the aromatic compound is formed according to β cleavage under electron impact, the carbon number of the alkyl side chain on the compound may be indicated by the following equation;

$$b=a(n-1)/n+1 \qquad (1)$$

where

b: the total carbon number of the alkyl side chain in the ion produced;
a: the total carbon number of the alkyl side chain in the original molecule, and
n: the alkyl side chain number.

If the ion is formed according to α cleavage, the equation will be:

$$b=a(n-1)/n \qquad (2)$$

The effects of the alkyl side chain number and the structure upon n values from Eqs. 1 and 2 have also been studied. From the study, a method has been devised by which the alkyl side chain number of aromatics in the high-boiling-range fraction of petroleum can be determined from the total carbon number of the alkyl side chain in the molecule ion and the carbon number of the alkyl side chain in the peak showing the most intense peak in the spectrum.

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[8] H. M. Grubb and S. Meyerson, " Mass Spectrometry of Organic Ions, " Academic Press, New York (1963), p. 457.

[9] E. M. Charlet, K. P. Lanneau and F. B. Johnson, Cleveland Meeting, Am. Chem. Soc., Petr. Div., 105, April, 1951.