An Investigation of Structure of Intermediate Ions by Kinetic Energy Release. $C_7H_7^+$ Ions from Several Derivatives of Toluene

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The amount of kinetic energy release accompanying the metastable ion reaction $C_7H_7^+ (m/z\ 91) \longrightarrow C_6H_5^+ (m/z\ 65) + C_2H_2$ has been determined for 24 derivatives of toluene by scanning electric sector voltage of a double focusing mass spectrometer.

Except for the case of benzyl methyl ether and benzyl chloride, the determined values were nearly equal to those for the $C_7H_7^+$ ions from toluene and isopropyl *o*-toluate, which are considered to produce the $C_7H_7^+$ ion of tropylium ion structure.

From the profile of metastable ion peak, the mechanism of the fragmentation reaction $C_7H_7I^{++} (m/z\ 218) \longrightarrow C_7H_7^+ (m/z\ 91) + I\cdot$ for *m*- and *p*-iodotoluenes has been estimated.

1. Introduction

Although it has been suggested¹⁾ that the validity of the use of kinetic energy release (KER) values for the determination of ion structure has remained unestablished, the KER values calculated from the metastable peak width play an important role in studying the structure and the fragmentation mechanism of various ions.²⁻⁹⁾ However, in analytical mass spectrometer, the metastable peak is sometimes interfered with other normal peaks making the KER values hardly determinable. To avoid this

disadvantage, using a double focusing mass spectrometer, the techniques of the ion accelerating voltage scan and the electric sector voltage scan have been reported.^{3,7)}

In the present study, a Hitachi RMU-7M double focusing mass spectrometer (Nier-Johnson geometry) was modified to measure the KER values by the electric sector voltage scan method. This paper describes the structures of the intermediate ion, $C_7H_7^+$, from 24 derivatives of toluene by measuring the KER values accompanying the metastable ion reaction (1). It also describes the fragmentation mechanism of

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m- and *p*-iodotoluene molecular ions into C_7H_7^+ ion by examining the profile of the corresponding metastable ion peak.

2. Experimental

In order to detect the fragment ions decomposed in the region between the earth slit and the electric sector, the electric sector voltage was scanned at a fixed ion accelerating voltage.^{2,7)} Further, a side-on type electron multiplier detector (Hamamatsu Television Co. Ltd.) was inserted behind the slit between the electric and magnetic sectors (β -slit) to detect the ion beam. When the normal mass spectra are measured, this electron multiplier detector can be taken out from the ion beam by driving a screw without breaking the vacuum.

The main beam width at half-height decreased with decreasing width of the entrance slit to the electric sector (α -slit), but it was approximately constant when the α -slit width was less than 0.25 mm. On the other hand, the metastable peak width at half-height was independent of the α -slit width, and main beam and the metastable peak widths were also independent of the width of the β -slit within 1.0 mm. Consequently, the KER values were taken with the α -slit set at 0.25 mm, and the β -slit set at 1.0 mm. The KER values, obtained with these experimental conditions, corresponding to the metastable ion reaction (1) for toluene were in good agreement with the values already known³⁾ (see Table I). Since the scanning speed of electric sector voltage was kept almost constant, the $\Delta E_{50\%}$, the

range of the voltage over which the peak is observed, can be obtained very easily from the metastable peak width at half-height. The KER values $T_{50\%}$ were calculated from the $\Delta E_{50\%}$ values by the following equation,^{2,7)} after correcting for the $\Delta E_{50\%}$ of the main beam of stable ions:

$$T_{50\%} = (m_1^2 \cdot eV) / (16m_2m_3) \cdot (\Delta E_{50\%}/E)^2 \quad (2)$$

where m_1 , m_2 and m_3 are the masses of a decomposing ion, a fragment ion and a neutral fragment, respectively, V (4800 volts) is ion accelerating voltage, and E (470 volts) is the sector voltage at which the main beam is seen.

Samples were introduced through an inlet system heated at 150°C. The temperature of the ion source was 200°C. The total emission current of the bombarding electron beam was 100 μA .

The samples (G. R grade products from Tokyo Kasei Kogyo) were used without further purification after checking the purity with the mass spectrometer.

3. Results and Discussion

$[\text{C}_7\text{H}_7]^+$ ions. Ever since the classic original work of Meyerson et al.,⁸⁾ many authors have studied the fragmentation and the structure of the C_7H_7^+ ions from various precursors by several different methods.⁹⁻¹⁵⁾ Beynon et al., have reported the KER values for the reaction (1) for several derivatives of toluene, and have concluded that the benzylic C_7H_7^+ ion was associated with the high kinetic energy release of about 46 meV, while the tropylium ion was associated with the kinetic energy release of about 30 meV.³⁾

To confirm this conclusion⁹⁾ and to test the reliability of the measurements by our modified instrument, the KER values for the reaction (1) for 24 derivatives of toluene were determined and compared with the data from the literature.⁹⁾ The KER values obtained in the present experiment are given in Table I. Each value

Table I. Kinetic Energy Release for $[C_7H_7]^+ \longrightarrow [C_5H_5]^+ + C_2H_2$

Compound	This work	Literature ⁹⁾
Toluene	$31.1 \pm 0.7 \text{ meV}$	$30 \pm 2 \text{ meV}$
<i>o</i> -Methoxy toluene	33.7 ± 2.7	34 ± 2
<i>m</i> -Methoxy toluene	34.5 ± 2.2	35 ± 2
<i>o</i> -Bromotoluene	38.4 ± 1.3	
<i>m</i> -Bromotoluene	32.7 ± 1.3	
<i>p</i> -Bromotoluene	34.6 ± 1.6	
<i>o</i> -Iodotoluene	29.2 ± 1.6	
<i>m</i> -Iodotoluene	32.7 ± 0.9	
<i>p</i> -Iodotoluene	35.7 ± 3.1	
<i>o</i> -Xylene	34.2 ± 2.6	
<i>m</i> -Xylene	34.3 ± 0.7	
<i>p</i> -Xylene	33.3 ± 1.5	
<i>o</i> -Nitrotoluene	28.4 ± 1.6	
<i>m</i> -Nitrotoluene	28.6 ± 1.1	
<i>p</i> -Nitrotoluene	28.0 ± 1.0	
<i>o</i> -Tolualdehyde	26.0 ± 1.1	
<i>m</i> -Tolualdehyde	29.7 ± 1.8	
<i>p</i> -Tolualdehyde	32.0 ± 1.5	
<i>m</i> -Methyl acetophenone	33.5 ± 0.9	
<i>p</i> -Methyl acetophenone	27.5 ± 1.0	
<i>o</i> -Toluic acid	37.5 ± 1.6	
Isopropyl <i>o</i> -toluate	32.6 ± 0.5	
Benzyl methyl ether	45.5 ± 2.5	44 ± 2
Benzyl chloride	50.8 ± 3.8	46 ± 2

represents an average taken from at least five measurements and the experimental errors were obtained by the standard deviation method.

The data obtained in this experiment agree quite well with those in the literature,⁹⁾ and therefore, our data are considered to be reliable. All these values, except for benzyl methyl ether and benzyl

chloride, are close to those for toluene and isopropyl *o*-toluate. It was estimated from the intensity ratios of IKE spectra for the processes, m/z 94 $\longrightarrow$ m/z 66, m/z 94 $\longrightarrow$ m/z 67, and m/z 94 $\longrightarrow$ m/z 68, in the deuterium labelled isopropyl *o*-toluate ($CD_3-C_6H_4COOCH(CH_3)_2$) that metastably decomposing m/z 91 ion from isopropyl *o*-toluate isomerizes to the tropylium ion prior to the decomposition into the m/z 65 ion.¹⁶⁾ The $C_7H_7^+$ ion from toluene has also been estimated to have the structure of the tropylium ion judging from the fragmentations of various kinds of deuterium labelled toluenes.^{8,12a)} Therefore, the $C_7H_7^+$ ions from all the compounds studied here, except for benzyl methyl ether and benzyl chloride, will isomerize to the tropylium ion prior to decomposition.

On the other hand, the $C_7H_7^+$ ion from benzyl methyl ether and benzyl chloride must be the benzyl ion according to Beynon et al.⁹⁾

$[C_7H_7I]^+ \longrightarrow [C_7H_7]^+ + \cdot I$ for *m*- and *p*-iodotoluenes. From the energetic consideration, Williams et al. have reported¹¹⁾ that chlorotoluene molecular ion undergoes ring expansion before the fragmentation $C_7H_7Cl^+ \longrightarrow C_7H_7^+ + \cdot Cl$ (reaction (a) in Scheme 1), while the molecular ions of bromo- and iodotoluene decompose into the m/z 91 ion without ring expansion (reaction (b) in Scheme 1). In contrast to this conclusion,¹¹⁾ McLafferty et al. have reported observing the collision activated (CA) spectra^{1,12b)} that only the ions from iodotoluene have retained the tolyl structure (D in Scheme 1). However, decomposing metastable ion intensity ratio has indicated^{13b)} that the $C_7H_7^+$ ions from bromo- and iodo-

toluenes isomerize into the tropylium ion prior to the decomposition.

The partial IKE spectrum of the reaction $C_7H_7I^+ \rightarrow C_7H_7^+ + I$ for *m*-iodotoluene is shown in Fig. 1. *p*-Iodotoluene also showed a similar metastable ion profile. It clearly indicates that two different mechanisms are involved in the reaction $C_7H_7I^+ \rightarrow C_7H_7^+ + I$ for *m*-iodotoluene. Taking

Scheme 1 Fragmentation mechanism of a halogenotoluene (X is a halogen atom).

Fig. 1. Partial IKE spectrum for *m*-iodotoluene showing the peak for the transition $218^+ \rightarrow 91^+$ (127).

the experimental results in the literatures^{1,12,13(b)} into consideration, these two fragmentation mechanisms may be the reaction (a) and (b) in Scheme 1.

We estimate that the part a in the metastable peak in Fig. 1 indicates the larger energy release reaction (a), while the part b indicates the smaller energy reaction (b) in Scheme 1, since, in general, the KER of a rearrangement reaction has been considered to be larger than that of simple cleavage reaction.^{17,18} In order to confirm this estimation, the ratios of the metastable ion intensities, b/a , were plotted as a function of nominal electron energy in Fig. 2. For simplicity, it is assumed that the metastable ion abundance a is the height from the base line to the inflection point of the metastable peak, and abundance b is the height from the inflection point to the top of the peak,

Fig. 2. Metastable ion intensity ratios, b/a (see Fig. 1), versus electron energy for the loss of iodine radical from the molecular ion of *m*-iodotoluene.

respectively (see Fig. 1).¹⁹⁾

From Fig. 2, it is obvious that the intensity ratio, b/a , decreases with decreasing electron energy. This supports the above mentioned estimation, since in the competing reaction, the critical energy for a rearrangement reaction (a) is usually smaller than that for a simple cleavage reaction (b).²⁰⁾ Consequently, the intensity ratio of a simple cleavage vs. a rearrangement reaction decreases with decreasing electron energy.²¹⁾

Unfortunately, the IKE spectra of $C_7H_7X^+ \longrightarrow C_7H_7^+ + \cdot X$ (where X is a halogen atom) in chloro- and bromotoluenes cannot be obtained accurately, because of a large amount of isotope in the molecular ion. Especially, in the case of chlorotoluene, the mass ratios of $(m/z\ 91)/(m/z\ 128)$ and $(m/z\ 65)/(m/z\ 91)$ are nearly equal interfering with the IKE peaks corresponding to $C_7H_7Cl^+ \longrightarrow C_7H_7^+ + \cdot Cl$ and $C_7H_7^+ \longrightarrow C_5H_5^+ + C_2H_2$.

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