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An Investigation of Structure of Intermediate Ions from Several Substituted Alkyl Benzoates by the *ortho* Effect and Kinetic Energy Release

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Single and double hydrogen atom transfers in reactions (1) and (2) are found in the mass spectra of n-propyl and n-butyl benzoates, and n-propyl and n-butyl p-hydroxybenzoates. In contrast, only single hydrogen atom transfer is found in the mass spectra of n-propyl and n-butyl salicylates and it is concluded that the hydrogen bond prevents the second hydrogen atom transfer. The kinetic energy release for the loss of water from the m/z 138 ion $[\text{C}_7\text{H}_6\text{O}_3]^+$ produced from ethyl and higher alkyl salicylates by a McLafferty rearrangement was nearly equal to that from the molecular ion of salicylic acid (m/z 138). The kinetic energy release for the loss of water from the m/z 137 ion $[\text{C}_7\text{H}_7\text{NO}_2]^+$ from ethyl o-aminobenzoate was also equal to that from the molecular ion of o-amino benzoic acid (m/z 137). However, the corresponding kinetic energy release from the m/z 136 ion $[\text{C}_8\text{H}_8\text{O}_2]^+$ from ethyl o-methylbenzoate was somewhat higher than that from the molecular ion of o-methyl benzoic acid (m/z 136).

Introduction

Information about the structure of intermediate ion plays an important role in studying the structure of the molecular ion and the fragmentation mechanism of ions. The structure of common intermediate ions from different precursors has been

examined by measuring the relative intensities of metastable peaks,¹⁻³⁾ kinetic energy releases,⁴⁻⁷⁾ and the heats of formation.⁸⁻¹¹⁾

It has been known that single and/or double hydrogen atom(s) transfer reactions (1) and (2) occur in ethyl and higher esters.¹²⁻¹⁴⁾ In the previous paper, it has

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been shown by the *ortho* effect¹⁵⁾ that the structure of intermediate ion $[\text{C}_6\text{H}_5\text{COOH}_2]^+$ (m/z 123) produced by

double hydrogen atoms transfer from several alkyl benzoates is the protonated benzoic acid structure with the hydrogen atom on the carbonyl group (structure a).

Continuing this work the present paper describes the fragmentation of n-propyl and n-butyl benzoates, n-propyl and n-butyl salicylates, and n-propyl and n-butyl p-hydroxybenzoates from the point of view of the *ortho* effect. It also describes the structures of $[\text{C}_7\text{H}_6\text{O}_3]^+$ ion (m/z 138) from alkyl salicylates, $[\text{C}_7\text{H}_7\text{NO}_2]^+$ ion (m/z 137) from ethyl o-aminobenzoate, and $[\text{C}_8\text{H}_8\text{O}_2]^+$ ion (m/z 136) from ethyl o-methylbenzoate by a McLafferty rearrangement by measuring kinetic energy release for the loss of water from these ions.

Experimental

The mass spectra and kinetic energy release were recorded with a Hitachi RMU-7M mass spectrometer. Samples were introduced via a heated inlet system 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 mass spectra were measured at 15 eV (vide infra). Kinetic energy releases were measured at 20 eV (vide infra). The ion

accelerating voltage was 4800 V.

The samples (E. P or G. R grade products from Tokyo Kasei Kogyo and Wako Pure Chemical Industries) were used without further purification after checking the purity with the mass spectrometer.

Metastable decomposition in the second field-free region was observed, and the kinetic energy release values $T_{50\%}$ were calculated¹⁶⁾ from the metastable peak width at half-height, after correction for the width of the main beam of stable ions.

Results and discussion

In order to investigate the fragmentation mechanism of alkyl benzoates from the point of view of the *ortho* effect, the mass spectra of n-propyl and n-butyl benzoates, n-propyl and n-butyl salicylates, and n-propyl and n-butyl p-hydroxybenzoates were studied. The mass spectra of the compounds studied are shown in Table 1 as $\% \Sigma$. As it is important in this paper to detect the existence of the m/z 139 ion produced by double hydrogen atoms transfer for n-propyl and n-butyl salicylates, the mass spectra were measured at 15 eV. Because it is generally known¹⁷⁾ that the activation energy of double hydrogen atoms transfer reaction is low, the relative abundance of this ion will be high at lower electron energy. The spectra were corrected for naturally occurring ^{13}C abundances.

In the mass spectra of n-propyl and n-butyl benzoates, the peaks at m/z 122 and m/z 123, which are produced by single and double hydrogen atom transfers in reactions (1) and (2), are strong. These peaks are expected to shift to m/z 138 and

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Table. 1. The mass spectra (15 eV) of alkyl benzoates, alkyl salicylates, and alkyl p-hydroxy benzoates (%Σ).

<i>m/z</i>	n-propyl benzoate	n-butyl benzoate	n-propyl salicylate	n-butyl salicylate	n-propyl p-hydroxy benzoate	n-butyl p-hydroxy benzoate
56		22.2		2.3		
57				3.1		
79		5.2				
92			3.6	1.7		
105	28.9	23.4				
120			55.2	54.2		
121			5.6	3.9	29.8	32.4
122	22.6	7.3			1.0	1.7
123	46.2	41.9				
135	1.2					
138			19.7	22.5	64.0	61.9
139			0.0	0.0	1.7	4.0
164	1.1					
180			15.9		3.5	
194				12.3		

m/z 139 for n-propyl and n-butyl salicylates, and n-propyl and n-butyl p-hydroxybenzoates, respectively. However, in the mass spectra of n-propyl and n-butyl salicylates, the *m/z* 138 peaks were very strong, but no *m/z* 139 peak was observed in a similar way to isopropyl and isobutyl salicylates.¹⁰⁾ As for n-propyl and n-butyl p-hydroxybenzoates, the peak at *m/z* 138 was the most abundant peak and, though small, a peak can be detected at *m/z* 139 in the both compounds.

For convenience the carbonyl oxygen atom is termed 1, and the other oxygen atom in the same carboxyl group is termed 2. For n-propyl and n-butyl p-hydroxybenzoates,

the hydrogen atom in the hydroxyl group cannot be attracted by either oxygen atom 1 or 2 of the carboxyl group. Thus the fragmentation pathways of these compounds may be similar to those of n-propyl and n-butyl benzoates, respectively, though there are slight differences, which may be attributed to the substituent effect¹⁸⁾ (see Table 1). On the other hand, for the neutral molecule of n-propyl and n-butyl salicylates, the hydrogen atom of the hydroxyl group at the *ortho* position may be attracted by oxygen atom 1 (the so-called intramolecular hydrogen bond)¹⁹⁾ (Scheme 1). Either of these oxygen atoms 1 and 2 may be ionized by electron impact. When oxygen atom 1 was ionized, the carboxyl group may rotate as shown in Scheme 1, because the hydrogen atom in the hydroxyl group has a partial positive charge, and it will repel a positive charge of oxygen

Scheme 1. Fragmentation pathways of n-propyl salicylate.

atom 1. In this case, the hydrogen atom in the hydroxyl group may be attracted by oxygen atom 2 (Scheme 1). If it is assumed that the hydrogen bond prevents the hydrogen atom transfer from alkyl group to the oxygen atom, which has a hydrogen bond, the fragmentation pathways of n-propyl and n-butyl salicylates can be shown as Scheme 1 by reference to the literature.^{15,20)} On the other hand, when oxygen atom 2 was ionized, the hydrogen bond may remain unchanged as it was in the neutral molecule. In this case, the m/z 138 ion may be produced from the molecular ion through four-membered ring.²¹⁾ An intense metastable peak for each fragmentation step was detected.

Consequently, if the above mentioned assumption is valid, it can be said on the mechanism of double hydrogen atoms transfer for n-propyl and n-butyl benzoates,

and n-propyl and n-butyl p-hydroxybenzoates that one hydrogen atom transfers from the alkyl group to oxygen atom 1 of the carbonyl group and another hydrogen atom transfers from the alkyl group to oxygen atom 2 of the same carboxyl group in the same manner as isopropyl and isobutyl compounds.¹⁵⁾ If this was not so, the m/z 139 peak by double hydrogen atoms transfer should be detected in the mass spectra of n-propyl and n-butyl salicylates. Therefore, the structure of the $[C_7H_7O_3]^+$ ion (m/z 139) produced by reaction (2) for alkyl p-hydroxybenzoate should be a rather than b. This is the same conclusion as in the literatures.¹²⁻¹⁵⁾ The fragmentation pathways of n-propyl p-hydroxybenzoates are shown in Scheme 2.

In order to examine the structure of the common intermediate ions from the different precursors, the kinetic energy

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Scheme 2. Fragmentation pathways of n-propyl p-hydroxybenzoate.

Fig. 1. Kinetic energy release values versus electron energy for the loss of water from the molecular ion of o-methyl benzoic acid and the $[\text{C}_8\text{H}_8\text{O}_2]^+$ ion from ethyl o-methylbenzoate.

release values were measured. The kinetic energy release for the loss of water from the molecular ion of o-methyl benzoic acid and the $[\text{C}_8\text{H}_8\text{O}_2]^+$ ion (m/z 136) from ethyl o-methylbenzoate is plotted against the electron energy in Fig. 1. It can be seen that the kinetic energy release is relatively constant when the electron energy is changed, as to be expected by QET.²²⁾

At lower electron energy, the abundance of metastable ion is very weak, whereas at higher electron energy, the metastable peak is masked by other normal peaks, and the kinetic energy release could not be determined exactly in the both cases. Consequently, taking the experimental results shown in Fig. 1 into consideration, the kinetic energy releases were measured

at 20 eV. The kinetic energy releases measured for the loss of water for several compounds are shown in Table 2 with the literature values.¹⁹⁾ For o-hydroxyl compounds, the kinetic energy releases for the loss of water from the m/z 138 ion $[\text{C}_7\text{H}_6\text{O}_3]^+$ from ethyl, n-propyl, isopropyl, n-butyl, isobutyl, and isoamyl salicylates are nearly equal to that of the molecular ion of salicylic acid. Thus, it can be said that the m/z 138 ions $[\text{C}_7\text{H}_6\text{O}_3]^+$ from ethyl and higher alkyl salicylates isomerize to the molecular ion of salicylic acid before the water elimination. It would be expected that the molecular ion of salicylic acid is to be in the keto-form.⁵⁾ Therefore, the loss of water from the m/z 138 ion from ethyl and higher alkyl salicylates is writ-

Table 2. Kinetic energy (meV) released for the loss of water at 20 eV.

Compounds	Transition	Observed ^{a)}	Literature values ¹⁹⁾	
salicylic acid	138 $\longrightarrow$ 120	9.3 $\pm$ 0.9	7 $\pm$ 1 ^{b)}	14 ^{c)}
ethyl salicylate	138 $\longrightarrow$ 120	10.2 $\pm$ 0.7		
n-propyl salicylate	138 $\longrightarrow$ 120	7.2 $\pm$ 0.4		
isopropyl salicylate	138 $\longrightarrow$ 120	5.5 $\pm$ 0.5		
n-butyl salicylate	138 $\longrightarrow$ 120	9.9 $\pm$ 0.5		
isobutyl salicylate	138 $\longrightarrow$ 120	10.3 $\pm$ 0.2		
isoamyl salicylate	138 $\longrightarrow$ 120	9.6 $\pm$ 0.2		
o-amino benzoic acid	137 $\longrightarrow$ 119	18.9 $\pm$ 1.4	14 $\pm$ 1	27
ethyl o-aminobenzoate	137 $\longrightarrow$ 119	21.6 $\pm$ 0.5		
o-methyl benzoic acid	136 $\longrightarrow$ 118	84.8 $\pm$ 2.4*	61 $\pm$ 4	94
ethyl o-methylbenzoate	136 $\longrightarrow$ 118	110.4 $\pm$ 4.5*		

a) Each value represents an average taken from at least five measurements and the given experimental errors are standard deviations.

b) Measured at 70 eV with a Hitachi RMU-6D double focusing mass spectrometer.

c) Measured at 70 eV with a A.E.I. MS-9 mass spectrometer.

*) Measured at 21 eV.

ten as Scheme 1.

For o-amino compounds, the kinetic energy release for the loss of water from the m/z 137 ion $[C_7H_7NO_2]^+$ from ethyl o-aminobenzoate is also equal to that of the molecular ion of o-amino benzoic acid. Therefore, the same conclusion mentioned above is led.

On the other hand, for o-methyl compounds, the kinetic energy release for the loss of water from the m/z 136 ion $[C_8H_8O_2]^+$ for ethyl o-methylbenzoate is about 25 meV higher than that of o-methyl benzoic acid (Table 2). This means that the m/z 136 ion from ethyl o-methylbenzoate does not isomerize to the molecular ion of o-methyl benzoic acid before the water elimination, or that the m/z 136 ion isomerize to the molecular ion of o-methyl benzoic acid, but the m/z 136 ion is to be in an excited state. If the latter case is valid, its energy of the excited state is about 0.5 eV higher than that of the ground state. This energy is roughly estimated by use of the formula²³⁾ $E = T \times 0.44 \times S$, where for the present case $S = 48 =$ number of oscillators in the activated complex of the molecular ion of o-methyl benzoic acid, and $T = 110 - 85 = 25$ meV (at 21 eV) = the difference between the kinetic energy releases.

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Keywords

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