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Doubly Charged Ion Mass Spectra of Monosubstituted Aromatic Compounds

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The 2E doubly charged ion mass spectra of twelve simple monosubstituted aromatic compounds were recorded. The spectral pattern of these compounds can be classified into three types. When the substituent is strongly electron-donating such as the amino or dimethylamino group, a very intense molecular ion peak appears, no fragment ion peak being observed. Phenol, anisole, toluene, and chlorobenzene show both molecular and fragment ion peaks in varying intensities. The parent benzene itself behaves similarly. Only fragment ion peaks were observed for nitrobenzene and aromatic carbonyl compounds such as benzaldehyde, acetophenone, methyl benzoate, or benzoic acid. The major fragmentation reactions are discussed.

In the 2E doubly charged ion mass spectrum[1,2] we can observe singly charged ions arising from the charge exchange reaction between doubly charged ions and any neutral species in the first field-free region of a mass spectrometer. Under these spectral conditions, aromatic hydrocarbons[3,4] exhibit several peculiar fragmentations including drastic skeletal changes, the spectra showing strong similarity irrespective of hydrocarbon structure. On the other hand, the spectra of aromatic amines[5] and substituted aromatic carbonyl compounds[6] afford certain characteristic fragmentation patterns with structures. The purpose of the present work is to investigate the structure-spectrum correlation in more detail by using simple monosubstituted aromatic compounds.[7]

General Appearance of the Spectrum

The 2E spectra of twelve simple aromatic compounds are given in Table 1 and Fig. 1. The spectral pattern of these compounds can be classified into three types. When the substituent is strongly electron-donating such as the amino or dimethylamino group, a very intense molecular ion peak appears, no fragment ion peak being observed. This indicates that the substituent can accomodate two positive charges within the benzene ring and the molecular ion is stable enough to be detected.

The compounds with other electron-donating substituents, *e.g.*, phenol, anisole, or toluene, show both molecular and fragment ion peaks in varying intensities. The parent benzene itself behaves similarly. Chlorobenzene, in which the substituent is electron-withdrawing, also exhibits a strong molecular ion peak as well as several fragment ion peaks of comparable intensity. In this case, the presence of lone-pair

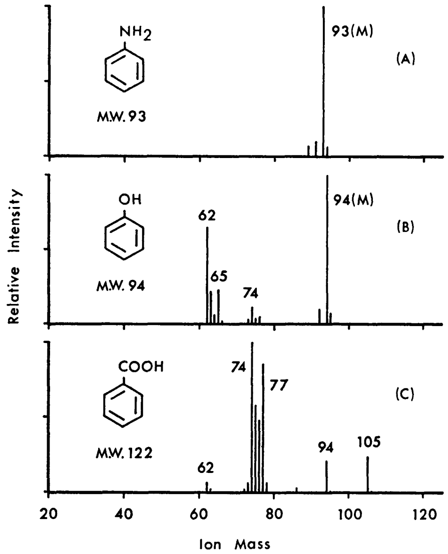

Fig. 1. 2E Doubly charged ion mass spectra of aniline (A), phenol (B), and benzoic acid (C).

TABLE 1. 2E DOUBLY CHARGED ION MASS SPECTRA OF MONOSUBSTITUTED AROMATIC COMPOUNDS[a)]
(RELATIVE INTENSITIES IN PARENTHESES)

C_6H_5-Z	[M]	[M-1]	$H\text{-}\overset{+}{C}(=C=)_x\overset{+}{C}\text{-}H$	Other fagment ion peaks
Z = $N(CH_3)_2$	121 (100)	120 (34)	74 (3)	104 (7), 117 (10), 119 (11), 122 (8)
OCH_3	108 (22)	—	62 (100), 74 (23)	63 (31), 64 (7), 65 (18), 75 (9), 79 (5)
CH_3	92 (21)	91 (38)	62 (3), 86 (43)	85 (3), 87 (10), 88 (7), 89 (6), 90 (100)
H	78 (100)	77 (8)	62 (3), 74 (74)	73 (5), 75 (44), 76 (46), 79 (8)
Cl	112 (100) 114 (31)	—	74 (44)	75 (33), 76 (79), 77 (5), 110 (5), 113 (6)
NO_2	123[b)]	—	62 (38), 74 (100)	63 (7), 73 (5), 75 (55), 76 (15), 77 (8), 87 (12), 89 (5), 93 (6), 102 (4)
CHO	106 (8)	105 (5)	62 (6), 74 (100), 86 (39)	73 (7), 75 (40), 76 (39), 77 (39), 78 (34), 85 (6), 87 (9), 90 (5), 104 (6)
$COCH_3$	120[b)]	—	74 (22), 86 (28), 98 (14)	75 (19), 76 (21), 77 (100), 87 (9), 91 (10), 99 (5), 102 (17), 105 (34)
$COOCH_3$	136[b)]	—	62 (4), 74 (79)	73 (7), 75 (62), 76 (51), 77 (100), 78 (10), 105 (13), 118 (10)

a) Spectra of aniline, phenol, and benzoic acid are shown in Fig. 1. b) No molecular ion peak was observed.

electrons on the chlorine atom seems to be a dominant factor for stabilization of two positive charges.

On the other hand, only fragment ion peaks were observed for nitrobenzene and aromatic carbonyl compounds such as benzaldehyde, acetophenone, methyl benzoate, or benzoic acid. Since the substituents of these compounds are electron-withdrawing, two positive charges are not stable in the molecular framework. This might be responsible for the exclusive occurrence of fragmentations.

Major Fragmentation Patterns

Two peaks which might be due to the ions of $[M-H_2]$ and $[M-2H_2]$ appear in the spectra of aniline and *N*,*N*-dimethylaniline. These ions were also observed in the substituted aniline derivatives.[6] The $[M-H]$ peak in *N*,*N*-dimethylaniline is also significant. On the other hand, phenol and anisole gave fragment ions at 62, 63, 64, and 65 mass units with expulsion of oxygen-containing fragments. In contrast to the case of aromatic amines,[5] elimination of hydrocarbon fragments does not seem to be very favorable for these compounds. Thus, the behavior of phenol and anisole seems to be similar to that in the ordinary singly charged ion spectrum.

The fragmentation of benzene and toluene has been discussed in detail in a previous paper.[4] Thus, the ions at 74 for benzene and 86 for toluene correspond to the allene-type dication of $\mathrm{H{-}\overset{+}{C}({=}C{=})_{\mathit{x}}\overset{+}{C}{-}H}$ with x being 4 and 5, respectively. This series of hydrocarbon ions may appear at 62, 74, 86, 98, *etc.* The peak at 86 is usually observed if the compound has a side chain containing at least one carbon atom directly bound to an aromatic ring. The $[M-H]$ and $[M-H_2]$ peaks were also prominent in benzene and toluene spectra.

Chlorobenzene showed a group of peaks at 74, 75, and 76 mass units as in benzene. These peaks are also characteristic of nitrobenzene and carbonyl compounds. Besides the usual ions of $[M-NO]$ and $[M-NO_2]$, a moderately intense peak at 62 mass units appeared in the nitrobenzene spectrum. The origin of this peak would be the same as in phenol and anisole.

For aromatic carbonyl compounds, C_6H_5–CO–R, two successive fragmentations, $[M-R]$ and $[M-R-CO]$, which eventually give rise to a phenyl ion at 77, were commonly observed as in the ordinary mass spectrum.

On the other hand, the $[M-CO]$ peak was also noticeable in the spectrum of benzaldehyde or benzoic acid (peaks at 78 and 94 mass units, respectively). This is ascribable to the novel fragmentation that involves a rearrangement reaction of the side chain, the peak being encountered in most of the *para*- and some of the *meta*-substituted aromatic carbonyl compounds.[6,8] Acetophenone and methyl benzoate exhibited a weak $[M-H_2O]$ peak. The mechanism of this fragmentation is obscure.

From these results, it is apparent that the fragmentation patterns of simple aromatic compounds clearly reflect the nature of the substituent. However, we have no evidence for the mechanism of these fragmentations. Due to the unusually drastic skeletal changes, the mechanistic interpretation in the 2E mass spectra may not be straightforward as in the ordinary mass spectra. Another difficulty in analyzing the fragmentation in the 2E spectrum is the involvement of collisional charge exchange process during the course of formation of each fragment ion. The relative intensities of individual peak should be examined with care, as Ast and Beynon have pointed out.[5] Empirically, however, the 2E doubly charged ion mass spectrum may prove useful in obtaining information on the structure of unknown compounds, or in discriminating the isomer pairs of certain molecules.[6]

Experimental

Materials. Commercial compounds were used. All the samples were characterized and checked for purity by conventional mass spectrometry prior to the determination of doubly charged ion mass spectra.

Doubly Charged Ion Mass Spectra. The spectra were recorded with an Hitachi RMU-7 double focusing mass spectrometer by the method previously described.[4] Standard operating conditions were as follows: ionizing energy 70 eV, ionizing current 80 μA, source temperature 250 °C, sample pressure $1-5\times10^{-6}$ Torr, and accelerating voltage 1.8 kV.

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