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## Ion Kinetic Energy Spectroscopy Study of Doubly Charged Ion Reactions in Some Mono and Disubstituted Benzenes\*

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The technique of ion kinetic energy spectroscopy was used to study the doubly charged metastable ion decompositions in a number of simple mono and disubstituted benzenes. Metastable decompositions of doubly charged ions were compared with the corresponding decompositions of singly charged ions. The kinetic energy released in all reactions in which doubly charged ions fragment to give two singly charged ions was measured and the corresponding inter-charge distances calculated. The structural inferences of these results are discussed.

### INTRODUCTION

Although the presence of doubly charged ions in mass spectra was observed as early as 1930<sup>1</sup>, the literature on mass spectrometric studies of doubly charged ions is extremely scanty. This apparent lack of interest is mainly due to the experimental difficulties involved: in conventional mass spectra, the peaks of doubly charged ions are usually weak and often coincide with singly charged ions of half the mass. Additional problems arise when metastable decompositions of doubly charged ions are concerned: these peaks are always extremely weak and spread over a few mass numbers; therefore, they will in most cases be indistinguishable in the midst of strong singly charged ion peaks in the mass spectra.

The technique of ion kinetic energy spectroscopy (IKES) introduced by Beynon et al. in 1969<sup>2</sup> opened new prospects for the studies of doubly charged ions. By adjusting the experimental parameters of a double focusing mass spectrometer, and by introducing an additional detector behind the electric sector, it was shown that doubly charged ions and their metastable decompositions could be conveniently studied without interference from singly charged ions. Examples of applications of IKES technique include plotting of pure doubly charged ion mass spectra<sup>3</sup>, plotting the IKE spectra which represent all of the doubly charged ion metastable decompositions<sup>4</sup>, studies of individual metastable decompositions with respect to the kinetic energy released<sup>5</sup>, studies of charge exchange and charge stripping reactions<sup>6</sup>, etc. For a more compre-

\* A part of the results was presented at 7<sup>th</sup> Int. Mass Spectrometry Conf., Florence, Aug. 30 — Sept. 3, 1976.

hensive coverage of the field of ion kinetic energy spectroscopy, the reader is referred to the only monograph on that subject<sup>7</sup>, as well as to some recent reviews<sup>8</sup>.

The knowledge and understanding of the chemistry of doubly charged ions, their reactions, structures and energetics are markedly inferior to the corresponding understanding and knowledge of singly charged ions. It is our belief that the systematic study of the behaviour of doubly charged ions could greatly help to enlighten the whole complex field of gaseous ion chemistry; in some case by providing similar, but additional, information to that obtained in studies of singly charged ions, and others by yielding unique data which cannot be obtained from single charged ion studies (e. g. interchange distances).

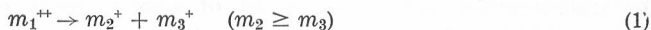
In this work, we have attempted to examine in some detail the metastable decompositions of doubly charged ions from a number of simple mono and disubstituted benzenes. The monosubstituted compounds studied were toluene, aniline and phenol, and the disubstituted analogs were three isomers each of xylene, diaminobenzene and dihydroxybenzene. It was our intention to identify the main metastable fragmentations of doubly charged ions and compare them with those of the singly charged ions, to evaluate the role of the substituent identity on the behaviour of doubly charged ions, to measure the energy released in the main metastable decompositions and to try to infer structural information from those measurements; also, we were interested in comparing the behaviour of isomeric compounds, knowing the similarities they exhibit in their singly charged ion studies.

#### EXPERIMENTAL

The experiments were performed on a CEC 21—110C double focusing mass spectrometer which was modified for IKES work by decoupling the accelerating voltage and the electric sector voltage and by introducing an additional detector behind the electric sector ( $\beta$ -position). Both accelerating voltage and electric sector voltage could be continuously scanned at variable rates. Ion source conditions employed were 150  $\mu$ A ionizing current, 70 eV\* ionizing energy and a temperature of about 100 °C. Sample introduction was made through an all glass inlet system maintained at about 150 °C.

#### *Ion Kinetic Energy Spectroscopy*

When a doubly charged ion decomposes in the first field free region of a double focusing mass spectrometer to give two singly charged ions



the product ion  $m_2^+$  will not have the right kinetic energy-to-charge ratio to be transmitted through the electric sector set at its normal value  $E$ . Therefore, these metastable decompositions will not be recorded in the mass spectra obtained in the standard way, i. e. under accelerating voltage  $V$  and electric sector voltage  $E$  conditions. If, however, the electric sector voltage is set to a new value  $(2m_2/m_1)E$ , maintaining the accelerating voltage constant at  $V$ , it is *only* the  $m_2^+$  ions of reaction (1) which will have the right kinetic energy-to-charge ratio to be transmitted. All other ions, including the main beam of singly charged ions, will not be transmitted under these conditions. When a detector is lowered into the ion beam immediately following the electric sector, a peak will be recorded representing reaction (1). If now the electric sector voltage is continuously scanned from the value  $E$  to the value  $2E$ , all product ions  $m_2^+$  of metastable decompositions represented by reaction (1) will be recorded at the detector as a series of peaks. The resulting spectrum is called an ion kinetic energy spectrum, or IKE spectrum.

In just the same way, products of metastable decompositions of singly charged ions

\* 1 eV =  $1.60219 \times 10^{-19}$  J.



can be recorded, but in that case, the electric sector voltage is to be scanned from the value 0 to the value  $E$ ; the peak due to reaction (2) will now appear at the value  $m_2/m_1 E$  and also peaks corresponding to formation of  $m_3^+$  by process (1). The IKE spectrum representing processes (1) is usually referred to the »high IKE spectrum«, while the one representing processes (2) is termed the »low IKE spectrum«.

From the above considerations, it is seen that the position of a peak in the IKE spectrum is determined by the  $m_2/m_1$  ratio for the process; since more than one reaction can have the same ratio, the transitions are not uniquely defined on the basis of IKE spectra alone. Also, some decompositions giving products of very similar kinetic energies may give incompletely resolved peaks in the IKE spectra. For these reasons, it is necessary to perform mass analysis of each IKE peak. To do this, a particular IKE peak is tuned on the  $\beta$ -detector, the detector is then raised out of the beam and the ions passed through the magnetic sector. By scanning the magnet, a mass spectrum will be recorded at the final detector, which will reflect all  $m_2^+$  ions giving rise to that particular IKE peak. Now that we know the  $m_2/m_1$  ratio (the position of the peak in the IKE spectrum) and the mass of the product ion  $m_2^+$ , the decomposition(s) is uniquely defined. Details of this procedure have been described elsewhere<sup>6a,7</sup>.

In metastable decompositions in which a doubly charged ion breaks up to give two singly charged ions<sup>1</sup>, a large amount of internal energy is released as translational energy of the fragments because of the Coulombic repulsion of the two positive charges. Due to this effect, peaks are usually very broad, and the resulting discrimination in the  $z$ -direction (parallel with the direction of the magnetic field) gives rise to a dish-topped peak shape. By measuring the width of the dish-topped peak, the kinetic energy  $T$  released in the decomposition can be calculated<sup>9</sup>. If it is assumed that the Coulombic energy of repulsion between the two like charges ( $e$ ) is the only source of the kinetic energy released (to be discussed later), the effective intercharge distance  $R$  in the transition state can be calculated from the relationship

$$T = e^2/R \quad (3)$$

If there were only one discrete amount of kinetic energy released in the decomposition reaction (1), the sides of the dish-topped peak would be parallel, and it would be immaterial at which point along the peak its width was measured. However, since there is always some distribution of the energies released, the sides tend to exhibit more or less of a slope; this effect may be enhanced by instrumental parameters, as well. Furthermore, there is always some distribution of energies inherent in the decomposing  $m_1^{++}$  ions. Under these circumstances, the questions arises as to where the peak width should be measured. We have taken width measurements at the top of the wings, which was the approach taken in most of the studies previously reported<sup>4a-c,5b,6a</sup>. However, a recent study has used measurement of peak widths at half-height<sup>10</sup>, which may alter the resulting  $T$  values for some peaks. While there is no sound theoretical justification for favoring either of the above two procedures, it is essential to maintain consistency in the way measurements are taken and always to state clearly which method was used.

#### RESULTS AND DISCUSSION

Low and high IKE spectra were plotted for all compounds and the major IKE peaks were mass analyzed. The main metastable decompositions that have thus been identified are listed in Tables I—VI. It should be emphasized that these lists are not intended to be comprehensive; only the main transitions were considered. This is particularly true for metastable decompositions of singly charged ions, which are numerous, but whose detailed study was not the objective of this work; only a few of the most intense ones were picked out for comparison purposes. Kinetic energy release  $T$  values were calculated for all decompositions of doubly charged ions; these are also listed in the tables together with the corresponding intercharge distances  $R$ , as obtained from equation (3).

TABLE I  
Main Metastable Decompositions in Toluene<sup>a</sup>

Singly charged ions	Doubly charged ions	Position in the IKE spectrum	T/eV	R/Å
92 <sup>+</sup> → 66 <sup>+</sup> + 26 (s) <sup>b</sup>	92 <sup>++</sup> → 77 <sup>+</sup> + 15 <sup>+</sup> (w)	1.67 E	2.7	5.3
91 <sup>+</sup> → 65 <sup>+</sup> + 26 (s)	92 <sup>++</sup> → 66 <sup>+</sup> + 26 <sup>+</sup> (w)	1.43 E	2.7	5.3
77 <sup>+</sup> → 51 <sup>+</sup> + 26 (m)	92 <sup>++</sup> → 65 <sup>+</sup> + 27 <sup>+</sup> (w)	1.41 E	2.8	5.1
65 <sup>+</sup> → 39 <sup>+</sup> + 26 (m)	92 <sup>++</sup> → 64 <sup>+</sup> + 28 <sup>+</sup> (w)	1.39 E	3.0	4.8
	92 <sup>++</sup> → 53 <sup>+</sup> + 39 <sup>+</sup> (w)	1.15 E	3.4	4.2
	91 <sup>++</sup> → 76 <sup>+</sup> + 15 <sup>+</sup> (w)	1.67 E	2.7	5.3
	91 <sup>++</sup> → 65 <sup>+</sup> + 26 <sup>+</sup> (m)	1.43 E	2.6	5.5
	91 <sup>++</sup> → 64 <sup>+</sup> + 27 <sup>+</sup> (m)	1.41 E	2.9	5.0
	91 <sup>++</sup> → 63 <sup>+</sup> + 28 <sup>+</sup> (w)	1.38 E	2.9	5.0
	91 <sup>++</sup> → 51 <sup>+</sup> + 39 <sup>+</sup> (s)	1.14 E	3.5	4.1
	90 <sup>++</sup> → 64 <sup>+</sup> + 26 <sup>+</sup> (w)	1.42 E	2.6	5.5
	90 <sup>++</sup> → 63 <sup>+</sup> + 27 <sup>+</sup> (s)	1.40 E	2.9	5.0
	89 <sup>++</sup> → 63 <sup>+</sup> + 26 <sup>+</sup> (w)	1.42 E	2.6	5.5

<sup>a</sup> Losses of H, H<sub>2</sub>, H<sup>+</sup> and H<sub>2</sub><sup>+</sup> have not been considered;

<sup>b</sup> Letters in parentheses denote relative intensities of transitions: (s) strong, (m) moderate, and (w) weak. These should be regarded only as very rough estimates for comparisons between transitions within one compound only; singly charged and doubly charged ions are compared separately.

TABLE II  
Main Metastable Decompositions in Aniline<sup>a</sup>

Singly charged ions	Doubly charged ions	Position in the IKE spectrum	T/eV	R/Å
93 <sup>+</sup> → 66 <sup>+</sup> + 27 (s) <sup>b</sup>	93 <sup>++</sup> → 78 <sup>+</sup> + 15 <sup>+</sup> (s)	1.68 E	2.3	6.3
92 <sup>+</sup> → 65 <sup>+</sup> + 27 (s)	93 <sup>++</sup> → 75 <sup>+</sup> + 18 <sup>+</sup> (m)	1.61 E	2.1	6.9
78 <sup>+</sup> → 52 <sup>+</sup> + 26 (w)	93 <sup>++</sup> → 65 <sup>+</sup> + 28 <sup>+</sup> (s)	1.40 E	4.0	3.6
76 <sup>+</sup> → 50 <sup>+</sup> + 26 (w)	93 <sup>++</sup> → 66 <sup>+</sup> + 27 <sup>+</sup> (w)	1.42 E	2.4	6.0
66 <sup>+</sup> → 39 <sup>+</sup> + 27 (w)	93 <sup>++</sup> → 54 <sup>+</sup> + 39 <sup>+</sup> (s)	1.16 E	3.1	4.6
66 <sup>+</sup> → 40 <sup>+</sup> + 26 (w)	92 <sup>++</sup> → 63 <sup>+</sup> + 29 <sup>+</sup> (w)	1.37 E	2.8	5.1
65 <sup>+</sup> → 39 <sup>+</sup> + 26 (w)	91 <sup>++</sup> → 63 <sup>+</sup> + 28 <sup>+</sup> (w)	1.38 E	3.1	4.6
	89 <sup>++</sup> → 61 <sup>+</sup> + 28 <sup>+</sup> (w)	1.37 E	2.9	5.0
	67 <sup>++</sup> → 38 <sup>+</sup> + 29 <sup>+</sup> (w)	1.13 E	2.9	5.0

<sup>a, b</sup> See Table I.

TABLE III  
Main Metastable Decompositions in Phenol<sup>a</sup>

Singly charged ions	Doubly charged ions	Position in the IKE spectrum	T/eV	R/Å
94 <sup>+</sup> → 66 <sup>+</sup> + 28 (s) <sup>b</sup>	94 <sup>++</sup> → 79 <sup>+</sup> + 15 <sup>+</sup> (s)	1.68 E	2.2	6.5
94 <sup>+</sup> → 55 <sup>+</sup> + 39 (w)	94 <sup>++</sup> → 75 <sup>+</sup> + 19 <sup>+</sup> (w)	1.60 E	2.4	6.0
93 <sup>+</sup> → 65 <sup>+</sup> + 28 (s)	94 <sup>++</sup> → 65 <sup>+</sup> + 29 <sup>+</sup> (s)	1.38 E	3.7	3.9
79 <sup>+</sup> → 51 <sup>+</sup> + 28 (w)	94 <sup>++</sup> → 55 <sup>+</sup> + 39 <sup>+</sup> (w)	1.17 E	3.1	4.6
77 <sup>+</sup> → 51 <sup>+</sup> + 26 (w)	94 <sup>++</sup> → 63 <sup>+</sup> + 31 <sup>+</sup> (w)	1.34 E	3.1	4.6
66 <sup>+</sup> → 40 <sup>+</sup> + 26 (m)	92 <sup>++</sup> → 63 <sup>+</sup> + 39 <sup>+</sup> (w)	1.37 E	2.9	5.0
65 <sup>+</sup> → 39 <sup>+</sup> + 26 (m)				

<sup>a, b</sup> See Table I.

TABLE IV  
Main Metastable Decompositions in *m*-Xylene<sup>a</sup>

Singly charged ions	Doubly charged ions	Position in the IKE spectrum	T/eV	R/Å
106 <sup>+</sup> → 91 <sup>+</sup> + 15 (s) <sup>b</sup>	106 <sup>++</sup> → 91 <sup>+</sup> + 15 <sup>+</sup> (m)	1.72 E	2.6	5.5
105 <sup>+</sup> → 79 <sup>+</sup> + 26 (m)	106 <sup>++</sup> → 79 <sup>+</sup> + 27 <sup>+</sup> (w)	1.49 E	3.2	4.5
91 <sup>+</sup> → 65 <sup>+</sup> + 26 (w)	105 <sup>++</sup> → 78 <sup>+</sup> + 27 <sup>+</sup> (s)	1.39 E	3.1	4.6
	104 <sup>++</sup> → 89 <sup>+</sup> + 15 <sup>+</sup> (w)	1.71 E	2.7	5.3
	102 <sup>++</sup> → 87 <sup>+</sup> + 15 <sup>+</sup> (m)	1.71 E	1.9	7.6
	102 <sup>++</sup> → 63 <sup>+</sup> + 39 <sup>+</sup> (w)	1.24 E	3.0	4.8

<sup>a, b</sup> See Table I.

TABLE V  
Main Metastable Decompositions in *m*-Diaminobenzene<sup>a</sup>

Singly charged ions	Doubly charged ions	Position in the IKE spectrum	T/eV	R/Å
108 <sup>+</sup> → 91 <sup>+</sup> + 17 (w) <sup>b</sup>	108 <sup>++</sup> → 90 <sup>+</sup> + 18 <sup>+</sup> (s)	1.67 E	1.4	10.1
108 <sup>+</sup> → 81 <sup>+</sup> + 27 (s)	108 <sup>++</sup> → 80 <sup>+</sup> + 28 <sup>+</sup> (s)	1.48 E	2.7	5.4
107 <sup>+</sup> → 80 <sup>+</sup> + 27 (w)	107 <sup>++</sup> → 73 <sup>+</sup> + 28 <sup>+</sup> (m)	1.48 E	2.5	5.8
92 <sup>+</sup> → 65 <sup>+</sup> + 27 (w)	106 <sup>++</sup> → 78 <sup>+</sup> + 28 <sup>+</sup> (m)	1.47 E	2.5	5.8
91 <sup>+</sup> → 64 <sup>+</sup> + 27 (w)	82 <sup>++</sup> → 54 <sup>+</sup> + 28 <sup>+</sup> (m)	1.32 E	3.0	4.7
80 <sup>+</sup> → 53 <sup>+</sup> + 27 (m)	81 <sup>++</sup> → 54 <sup>+</sup> + 27 <sup>+</sup> (w)	1.33 E	3.2	4.5
79 <sup>+</sup> → 52 <sup>+</sup> + 27 (w)	80 <sup>++</sup> → 54 <sup>+</sup> + 26 <sup>+</sup> (w)	1.35 E	2.8	5.1
	80 <sup>++</sup> → 52 <sup>+</sup> + 28 <sup>+</sup> (m)	1.30 E	3.3	4.3
	79 <sup>++</sup> → 52 <sup>+</sup> + 27 <sup>+</sup> (m)	1.32 E	3.5	4.1

<sup>a, b</sup> See Table I.

TABLE VI  
Main Metastable Decompositions in *m*-Dihydroxybenzene<sup>a</sup>

Singly charged ions	Doubly charged ions	Position in the IKE spectrum	T/eV	R/Å
110 <sup>+</sup> → 82 <sup>+</sup> + 28 (s) <sup>b</sup>	110 <sup>++</sup> → 91 <sup>+</sup> + 19 <sup>+</sup> (w)	1.65 E	2.3	6.3
110 <sup>+</sup> → 92 <sup>+</sup> + 18 (w)	110 <sup>++</sup> → 81 <sup>+</sup> + 29 <sup>+</sup> (s)	1.47 E	3.1	4.6
109 <sup>+</sup> → 81 <sup>+</sup> + 28 (s)	108 <sup>++</sup> → 79 <sup>+</sup> + 29 <sup>+</sup> (w)	1.46 E	2.5	5.8
92 <sup>+</sup> → 64 <sup>+</sup> + 28 (w)	92 <sup>++</sup> → 63 <sup>+</sup> + 29 <sup>+</sup> (m)	1.37 E	2.5	5.8
82 <sup>+</sup> → 54 <sup>+</sup> + 28 (m)	82 <sup>++</sup> → 63 <sup>+</sup> + 19 <sup>+</sup> (w)	1.54 E	2.5	5.8
81 <sup>+</sup> → 53 <sup>+</sup> + 28 (m)	82 <sup>++</sup> → 55 <sup>+</sup> + 27 <sup>+</sup> (w)	1.34 E	3.3	4.4
54 <sup>+</sup> → 39 <sup>+</sup> + 15 (m)	81 <sup>++</sup> → 52 <sup>+</sup> + 29 <sup>+</sup> (w)	1.28 E	3.2	4.5
	80 <sup>++</sup> → 51 <sup>+</sup> + 29 <sup>+</sup> (m)	1.28 E	3.0	4.8

<sup>a, b</sup> See Table I.

Disubstituted compounds are represented by only one isomer each, since there were no differences in *T* values greater than the experimental uncertainty for other isomers of all three compounds. The typical appearance of high IKE spectra is shown in Figure 1, which represents the high IKE spectra of *o*-, *m*- and *p*-dihydroxybenzene. The dish-topped peaks represent charge separation reactions of doubly charged ions, which are the object of this study. In addition,

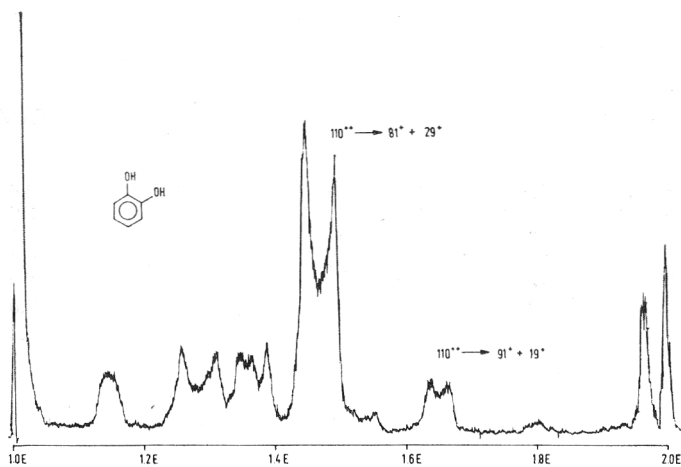


Fig. 1a

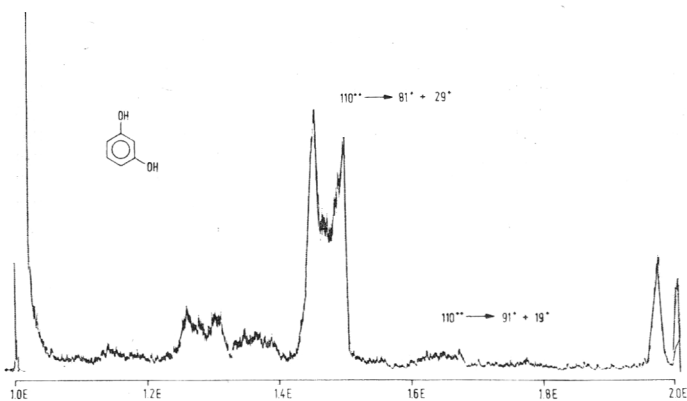


Fig. 1b

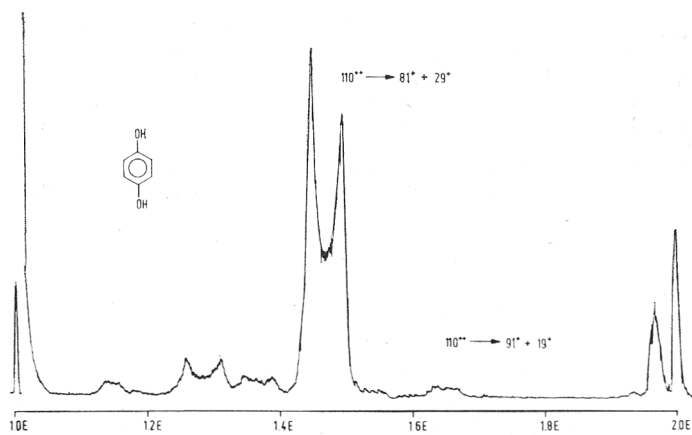


Fig. 1c

a few Gaussian peaks are evident. The peak at the electric sector voltage value of 1.0E represents the main beam of stable ions (it is plotted with low sensitivity). The peak at the value 2.0E is due to charge exchange processes of the type



where  $N$  denotes the neutral molecules of the residual gas in the mass spectrometer tube. Mass analysis of this peak yields the doubly charged ion mass spectrum of the compound<sup>3</sup>. The peak to the immediate left of the 2.0E peak represents a two step process, i. e. charge exchange followed by the loss of a hydrogen



The order of these processes could also be reversed, i. e. the loss of hydrogen could precede the charge exchange.

### Main Characteristics of IKE Spectra

(i) *Monosubstituted benzenes (Tables I—III).* — The low IKE spectra of toluene, aniline and phenol are largely dominated by a single metastable decomposition, i. e. the loss of  $C_2H_2$  (mass 26) in toluene, HCN (mass 27) in aniline and CO (mass 28) in phenol (Figure 2). Each of these lost neutral fragments represents a stable compound; the dominance of this transition is greatest in aniline, somewhat less in phenol, and least in toluene.

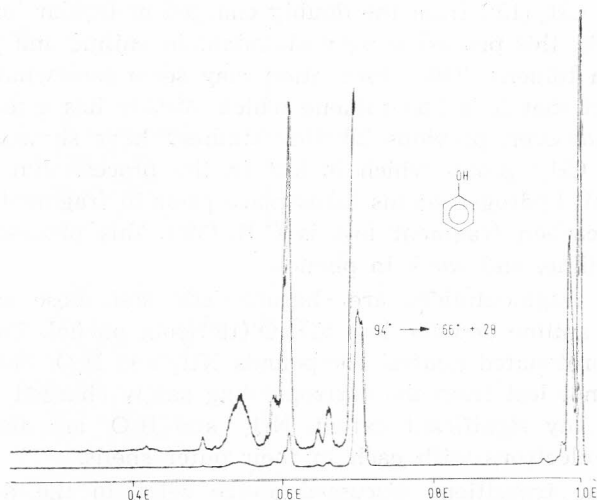


Fig. 2

It should be noted that the above three neutral fragments most favorably lost are all isoelectronic species, with 10 electrons each in their outer shells. The only other intense transition of singly charged ions is the loss of  $C_2H_2$  in all three compounds, which of course is the common fragmentation mode of the aromatic ring.

In the metastable decompositions of doubly charged ions (high IKE spectra), processes corresponding to those of singly charged ions are most prominent; the charged fragments lost represent the protonated neutral species:  $C_2H_3^+(27^+)$  in toluene,  $H_2CN^+(28^+)$  in aniline and  $HCO^+(29^+)$  in phenol (Figure 3). These three ions are of course still isoelectronic with each other, as well as with their neutral analogs, having 10 electrons each in their outer shells.

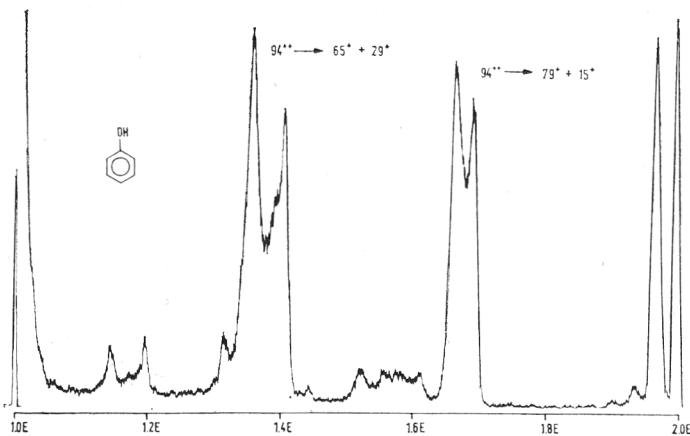


Fig. 3

The loss of  $CH_3^+(15^+)$  from the doubly charged molecular ion occurs in all three compounds; this process is very abundant in aniline and phenol (Figure 3), but weak in toluene. This observation may seem somewhat surprising in view of the fact that it is just toluene which already has a methyl group in its structure; however, previous labeling studies<sup>5c</sup> have shown that it is *not* the side chain  $CH_3^+$  group which is lost in the process, but that complete scrambling of all hydrogen atoms takes place prior to fragmentation. Another common hydrocarbon fragment lost is  $C_3H_3^+(39^+)$ ; this process is intense in toluene and aniline, and weak in phenol.

Two more fragmentations are characteristic and these are the loss of  $NH_4^+(18^+)$  from aniline and the loss of  $H_3O^+(19^+)$  from phenol. These ions again represent the protonated neutral compounds  $NH_3$  and  $H_2O$ , but these neutral fragments are not lost from the corresponding singly charged ions of aniline and phenol to any significant extent.  $NH_4^+$  and  $H_3O^+$  are also isoelectronic species with 8 electrons with each in their outer shells.

Most of the transitions discussed above refer to the doubly charged molecular ions, although, as can be seen from Tables I—III, some of the fragment ions also show similar decomposition reactions. It should be noted that in the case of toluene,  $M^{++}$  and  $(M-1)^{++}$  decompose in an identical way, but the processes from the  $(M-1)^{++}$  ion are much more intense. This parallels the situation encountered with the singly charged ions in toluene, thus suggesting that the  $C_7H_7$  tropylium ion is important both as a singly charged and as a doubly charged species.



(ii) *Disubstituted benzenes (Tables IV—VI).* — Introduction of the second functional group into the molecule causes significant changes in its decomposition pattern. The low IKE spectra of xylenes, diaminobenzenes and dihydroxybenzenes are still dominated by the loss of  $C_2H_2$ , HCN and CO, respectively. However, the new decomposition processes of the singly charged ions now involve losses of  $CH_3$  (mass 15) from xylenes,  $NH_3$  (mass 17) from diaminobenzenes and  $H_2O$  (mass 18) from dihydroxybenzenes. On the other hand, the loss of  $C_2H_2$  (mass 26), which was observed in all three monosubstituted compounds, is no longer evident, except in the case of xylenes.

The most intense peaks in the high IKE spectra represent the same losses as those observed in the doubly charged ions of monosubstituted compounds, i. e. fragmentations in which  $C_2H_3^+$ ,  $H_2CN^+$  and  $HCO^+$  are lost from the hydrocarbon, amino and hydroxy compounds, respectively. Here, again, the strongest peaks are due to the loss of these fragment ions from the doubly charged molecular ions of diaminobenzenes and dihydroxybenzenes, while it is the  $(M-1)^{++}$  ion of xylenes (Figure 4) which yields the most intense decomposition peak.

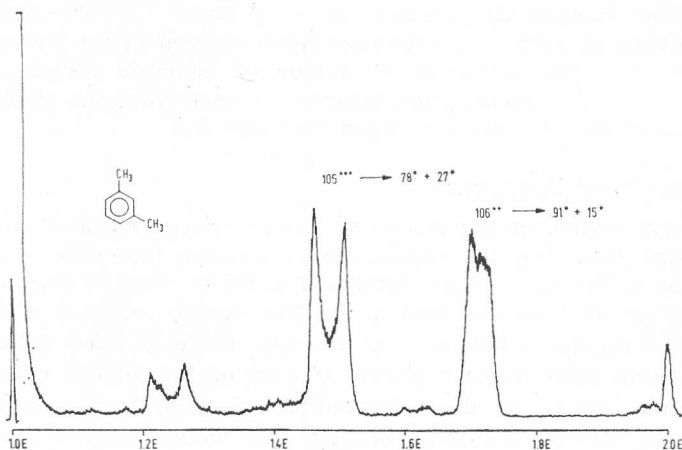


Fig-4

Also important are the losses of  $CH_3^+$  from xylenes,  $NH_4^+$  from diaminobenzenes and  $H_3O^+$  from dihydroxybenzenes; of these processes, the one in diaminobenzenes is most abundant, the one in xylenes has moderate intensity, while the loss of  $H_3O^+$  from dihydroxybenzenes is the weakest. As one might expect, the loss of the hydrocarbon fragment  $C_3H_3^+$  (39<sup>+</sup>) does not occur in the diamino and dihydroxy compounds, reflecting their reduced hydrocarbon character; it is still observed in xylenes, but only as a decomposition mode of the  $(M-4)^{++}$  ion.

Another aspect of the high IKE spectra of disubstituted compounds is the behaviour of isomers. Generally, since IKE spectra represent metastable decompositions, which are known to be much milder processes than decompositions in the ion chamber, one would expect that subtle structural differences might be better preserved and reflected in the IKE spectra, than in conventional

mass spectra. Indeed, distinguishing isomers on the basis of their low IKE spectra has been reported in the literature<sup>4b,c, 11a-d</sup>.

The high IKE spectra of compounds in this study did not show significant differences. The three isomers of xylene give practically identical high IKE spectra; in the case of diaminobenzenes, some minor differences in peak intensities were observed, but these could hardly constitute the basis for isomer identification. The largest differences have been found in the high IKE spectra of isomeric dihydroxybenzenes (Figure 1), where peak intensities show appreciable variation. However, the analytical value of this finding has little importance in view of the fact that even the conventional mass spectra of dihydroxybenzenes exhibit significant differences.

The fact that high IKE spectra of the isomers studied show great similarities suggests that the doubly charged ions undergo isomerization prior to decomposition. The mechanism of this process has not been established, but it could well be that it occurs via a 7 membered ring formed by introduction of one substituent group into the benzene ring. Formation of these 7 membered rings is well known for hydrocarbons, and it has also been reported for aromatic amino compounds (introduction of nitrogen into the ring). The fact that no evidence of such ring expansion with oxygen atoms exists, may well explain the somewhat different behaviour of isomeric dihydroxybenzenes. Further evidence for isomerization processes comes from the study of charge separation reactions of doubly charged ions (see below).

### *Charge Separation Reactions*

As already stated, measurement of kinetic energy released in metastable decompositions involving the separation of charges (reaction 1) enables the determination of the interchange distance  $R$  at the moment of decomposition (3). Since expression (3) assumes that all of the energy released is due only to the Coulombic repulsion between the charges, the calculated value of  $R$  will be the minimum interchange distance. If part of the energy released is due to the internal energy of the activated complex, or to the non-Coulombic portion of the reverse activation energy, this would need to be subtracted from the measured value of  $T$ , and this in turn would yield larger values for the interchange distance  $R$ . Since the above contribution to  $T$  is very small, seldom more than 0.1–0.2 eV, equating  $T = T_{\text{Coulombic}}$  is a fair approximation<sup>12</sup>.

The validity and usefulness of the concept of charge localisation in the molecular and fragment ions has been extensively debated in the mass spectrometry literature from its introduction<sup>12</sup> to the present time<sup>14</sup>. While there seem to be a lot of controversial arguments as concerning the validity of this concept is applied to singly charged ions, there is substantial evidence supporting the localisation of charges in doubly charged ions. The shape of the metastable dish-topped peaks points to the fact that there is essentially only one discrete amount of energy released in these transitions; if so, the charges must be localised at the moment of decomposition. The minimum energy requirement predicts that the two positive charges would tend to localise as far apart as possible; obviously, the most favorable locations in that respect

would be the two opposite ends of the ion. If that were the case, the interchange distance  $R$  would represent the length of the ion structure. Availability of such information should be of great significance in rationalisation of the ion structures. This approach was first used<sup>15</sup> in assigning a linear structure to the doubly charged benzene molecular ions, based on the fact that the reaction involves



release of 2.6 eV of energy. This corresponds to an interchange distance of 5.5 Å; since the diameter of the benzene ring is only 2.9 Å, the  $\text{C}_6\text{H}_6^{++}$  ion must have an open chain structure.

One can go a step further by assuming an average value of 1.2–1.3 Å as representing one bond length in doubly charged ions (some variation with the nature of the bond and degree of unsaturation is, of course, recognized). This would allow one to determine the number of bonds between the two charges, given the interchange distance  $R$ . Having in mind the approximations inherent in such an approach, as well as a certain measure of experimental uncertainty mentioned earlier, we estimate the overall uncertainty in charge separation value to be of the order of  $\pm 0.3$ – $0.5$  Å in most cases. In view of this fact, we believe that assignment of definitive structures would not be justified on the basis of interchange separation data alone; however, certain correlations and comparisons between ion structures, distinguishing between gross structural differences such as closed rings versus open chains, etc., can still be made. A few examples selected from the data obtained in this study are given below.

Examination of the charge separation data listed in Tables I–VI reveals the fact that there are numerous instances in which a particular ion is shown to exist in more than one reactive structural form, depending on the reactions involved. Some examples of this behaviour are presented in Table VII.

TABLE VII

*Examples of Different Interchange Distances in the Same Decomposing Ion as a Function of Fragment Lost*

Compound	Decomposing ion	Fragment(s) lost	$R/\text{Å}$
Phenol	$\text{M}^{++}$	29 <sup>+</sup> , 31 <sup>+</sup> , 39 <sup>+</sup>	3.9–4.6
		15 <sup>+</sup> , 19 <sup>+</sup>	6.0–6.5
Aniline	$\text{M}^{++}$	28 <sup>+</sup> , 39 <sup>+</sup>	3.6–4.6
		15 <sup>+</sup> , 18 <sup>+</sup> , 27 <sup>+</sup>	6.0–6.9
<i>m</i> -Xylene	$(\text{M}-4)^{++}$	39 <sup>+</sup>	4.8
		15 <sup>+</sup>	7.6
<i>m</i> -Diaminobenzene	$\text{M}^{++}$	28 <sup>+</sup>	5.4
		18 <sup>+</sup>	10.1
<i>m</i> -Dihydroxybenzene	$\text{M}^{++}$	29 <sup>+</sup>	4.6
		19 <sup>+</sup>	6.3

In each example cited, there seem to be two structurally different forms of the decomposing ion. One is tempted to conclude that the shorter interchange

distances involve intact ring structures, while the longer ones (all in excess of 6.0 Å) represent transitions from open chain structures. This may well be the case; however, it should be noted that in ions containing heteroatoms, there may be a tendency for the charge(s) to be localized on those sites<sup>16,4c</sup>; in such cases this effect may compete with the tendency of the charges to localize as far apart as possible. For that reason, short distances in ions containing heteroatoms do not *necessarily* mean that a ring structure is involved. The interchange distance of 10.1 Å obtained for the loss of 15<sup>+</sup> from the doubly charged molecular ion of *m*-diaminobenzene (same data were obtained for the other two isomers) is unusually large; it cannot be accounted for by the maximum of seven bonds available. The cause of this effect is not yet understood.

TABLE VIII  
Examples of Different Interchange Distances for Reactions in which Same Fragments are Lost

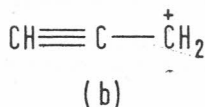
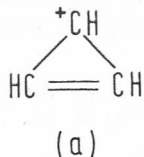
Compound	Reaction	R/Å
Aniline	93 <sup>++</sup> → 65 <sup>+</sup> + 28 <sup>+</sup>	3.6
	91 <sup>++</sup> → 63 <sup>+</sup> + 28 <sup>+</sup>	4.6
Phenol	94 <sup>++</sup> → 65 <sup>+</sup> + 29 <sup>+</sup>	3.9
	92 <sup>++</sup> → 63 <sup>+</sup> + 29 <sup>+</sup>	5.0
<i>m</i> -Dihydroxybenzene	110 <sup>++</sup> → 81 <sup>+</sup> + 29 <sup>+</sup>	4.6
	108 <sup>++</sup> → 79 <sup>+</sup> + 29 <sup>+</sup>	5.8
<i>m</i> -Xylene	106 <sup>++</sup> → 91 <sup>+</sup> + 15 <sup>+</sup>	5.5
	104 <sup>++</sup> → 89 <sup>+</sup> + 15 <sup>+</sup>	5.3
	102 <sup>++</sup> → 87 <sup>+</sup> + 15 <sup>+</sup>	7.6

Another interesting point is the change in ion structure which occurs upon loss of hydrogen atoms. In Table VIII a few examples have been depicted in which the same decomposition is involved from M<sup>++</sup> ions and (M - 2)<sup>++</sup> ions. The difference in the interchange distances measured for these processes suggests that significant structural changes take place upon the loss of two hydrogen atoms. This same effect is observed in xylenes only after four hydrogen atoms have been lost. This change may be due to the opening of the ring structure, but it could also represent a rearrangement of the already opened structure. For example, it has already been stated that the doubly charged molecular ion of benzene is a linear chain in the reaction in which it loses CH<sub>3</sub><sup>+</sup>, as indicated by the corresponding interchange distance of 5.5 Å. Doubly charged molecular ions of toluene and xylenes also lose CH<sub>3</sub><sup>+</sup>, the interchange distances remaining essentially constant, i. e. 5.3 and 5.5 Å, respectively. These results indicate that the same basic structure has been retained in toluene and xylenes to the one in benzene, which means that the extra carbon atom(s) must exist as branches on the main C<sub>6</sub> skeleton. However, the (M - 4)<sup>++</sup> ion in xylene yields an interchange distance of 7.6 Å for the same process of CH<sub>3</sub><sup>+</sup> loss; this is an indication that a rearrangement process has occurred whereby

the branched carbon atoms have been incorporated into the main skeleton, thus giving a linear chain of eight carbon atoms.

In contrast with the behaviour described above, neither toluene nor diaminobenzenes exhibit this effect (Tables I and V).

Recently<sup>10</sup>, the reaction  $91^{++} \rightarrow 52^+ + 39^+$  in toluene has been studied in detail and it was found that the resulting dish-topped peak is a composite one. The authors concluded that two processes are involved: in one,  $39^+$  is lost as a more stable cyclopropenyl ion (a) and this is accompanied by release of



3.73 eV of energy; in the other process, a less stable propargyl ion (b) is formed with the release of 3.18 eV of energy. Our measurements for the above reaction in toluene showed the release of 3.5 eV, but the resolution was inadequate to distinguish the two processes; therefore, we interpret this result as representing the average value of the kinetic energy release for both processes. However, the corresponding reactions in aniline and phenol both release 3.1 eV of energy which suggests that it is the less stable propargyl ion which is formed in those processes. These two energy releases are apparently comparable with the release of 3.18 eV energy measured in toluene.

The study of charge separation reactions in isomeric compounds may be a powerful tool in evaluating the isomerization processes in doubly charged ions. Different interchange distances for the corresponding processes in isomers should represent an indication that the structural individualities have been retained. On the contrary, identical interchange distances represent direct evidence that the doubly charged ions isomerise to a common structure or a mixture of structures before fragmentation. All isomeric doubly charged ions in this study have yielded identical interchange distances in corresponding processes (within experimental error); therefore, it is concluded that the doubly charged ions of xylenes, diaminobenzenes and dihydroxybenzenes all isomerise prior to decomposition. While this parallels the behaviour of singly charged ions in xylenes and diaminobenzenes, the isomerization of the doubly charged ions of *o*-, *m*- and *p*-dihydroxybenzenes is in contrast to the corresponding behaviour of their singly charged analogs, in which structural individualities of isomers are largely retained, as evidenced from both their mass and low IKE spectra.

#### CONCLUSION

Ion kinetic energy spectroscopy offers unique possibilities for the study of doubly charged ions without interferences from singly charged ions. High IKE spectra can be used for the systematic study of metastable decompositions of doubly charged ions; this type of analysis has been largely limited so far to singly charged ions, where it helped in understanding the various aspects of ion structures and fragmentation mechanisms. Similar prospects are now opened for doubly charged ions. A Mattauch-Herzog geometry instrument was used for the first time in this type of study and good sensitivity and fair energy resolution were obtained. Measurements of the kinetic energy release in

metastable decompositions of doubly charged ions, with the corresponding calculated interchange distances, enable certain structural characteristics of ions to be inferred. This technique is still in its infancy with a number of associated problems, but the inadequacies of the initial results should not be judged too severely, since it provides information not attainable by any other method. Less uncertainty in the values for interchange distances, together with some theoretical work on charge localisation and distribution phenomena would help in obtaining more definitive answers to the everintriguing questions concerning ion structures. Experiments in this field have so far all been limited to two or three laboratories; yet the initial results, in our opinion, are encouraging and well worth pursuing further.

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### IZVLEČEK

#### Študij reakcij ionov z dvema nabojeva s pomočjo spektrov kinetične energije ionov pri nekaterih mono in disubstituiranih benzenih

*T. Ast, M. Medved in J. Marsel*

S pomočjo spektrov kinetične energije ionov smo študirali razgradnje metastabilnih ionov z dvema nabojeva pri več mono in disubstituiranih benzenih. Razgradnje metastabilnih ionov z dvema nabojeva smo primerjali z ustreznimi razgradnimi reakcijami ionov z enim nabojem. Izmerili smo sproščene kinetične energije pri vseh razgradnih reakcijah, pri katerih se iz ionov z dvema nabojeva formirata dva iona z enim nabojem, in izračunali ustrezne razdalje med nabojeva. Na osnovi teh rezultatov smo naredili nekaj sklepov o strukturi ionov.

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