^{13}C Labelling Study of the Interconversion of Ethylbenzene, 7-Methylcycloheptatriene and *p*-Xylene Ions†

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The isomerization of the molecular ions of ethylbenzene, 7-methylcycloheptatriene and *p*-xylene by skeletal rearrangement prior to the formation of $[C_7H_7]^+$ ions has been investigated by using ^{13}C labelled compounds. The results obtained for ions generated by 70 eV and 12 eV electron impact, and fragmenting in the ion source, the 1st field free region and the 2nd field free region, respectively, are compared with those obtained from D labelled derivatives. It is shown that at long reaction times metastable *p*-xylene ions lose a methyl radical after scrambling of all C atoms and H atoms, while the unstable molecular ions in the ion source react by specific loss of one of the methyl substituents. Both unstable and metastable ethylbenzene ions fragment by two competing mechanisms, one corresponding to specific loss of the terminal methyl group, and the other involving scrambling of all C and H atoms. These results are discussed by use of a dynamic model developed for the mutual interconversion and fragmentation of the molecular ions of ethylbenzene, methylcycloheptatriene and *p*-xylene. The experimental results can be explained by an equilibrium between metastable methylcycloheptatriene ions and *p*-xylene ions with sufficient energy for skeletal rearrangement, while about 40% of the metastable ethylbenzene ions fragment after rearrangement to methylcycloheptatriene ions and about 60% of the ethylbenzene ions rearrange further to xylene ions before fragmentation. Metastable methylcycloheptatriene ions, mainly lose a methyl group without a skeletal rearrangement, however, because the rearranged ions are kinetically trapped as 'stable' xylene ions or ethylbenzene ions.

INTRODUCTION

Many unimolecular fragmentations of aromatic molecular ions are accompanied by extensive isomerization processes.[2] Since Rylander, Meyerson and Grubb[3] suggested the tropylium ion structure for $[C_7H_7]^+$ ions a considerable number of detailed studies[2] using isotopic labelling and other mass spectrometric techniques have been concerned with the reactions of benzyl and cycloheptatrienyl derivatives to $[C_7H_7]^+$ ions.

With respect to *ethylbenzene* (**1a**), *7-methylcycloheptatriene* (**2a**) and *p-xylene* (**3a**) ions these studies established a picture of extensive interconversion between molecular ions of **1a** and **2a** prior to fragmentation, while *p*-xylene ions of structure **3a** were believed to react in a rate-determining step to **2a** ions followed by loss of CH_3 and formation of $[C_7H_7]^+$ ions **b**. However, the results obtained from labelled derivatives of **1a**, **2a** and **3a**[4,5] are difficult to explain in detail, and are in conflict with the conclusions drawn from an investigation of kinetic energy release[6] during fragmentation.

Recently, a dynamic model[7] has been developed for the interconversion and fragmentation of ions **1a**, **2a** and **3a** to obtain a better insight into this complicated reaction system. The basis of this model is given by the *m*inimum *e*nergy *r*eaction *p*ath (MERP) for the rearrangements and fragmentations of these ions, calculated by the MNDO program,[8] in close analogy to the work of Dewar and Landman[9] on the interconversion of toluene and cycloheptatriene ions. In the present case, MNDO has been used instead of MNDO/3,[9] because the former method gives better results with respect to the influence of the additional methyl group at the aromatic nucleus. The investigation of the reaction paths leads to two different MERPs for two different rearrangement mechanisms, again in close analogy to the isomerization of toluene and cycloheptatriene ions.[9b] The first mechanism starts by migration of one of the α-H atoms in ions **1a** or **3a** to the *ipso* position of the aromatic ring (MERP A in *loc. cit.* 7), and the other by migration of the α-H atom to the *ortho* position (MERP B in *loc. cit.* 7, see Scheme 1).

MERP B (Fig. 1) which will be used in the following discussion shows two energy barriers of nearly the same height for both reactions $[\mathbf{1a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ and $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$, corresponding to the transition states **g** or **i** for $[\mathbf{1a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ and **m** or **o** for $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$. The potential energy of these transition states is definitely smaller than the potential energy of the products formed from **1a** ions by direct cleavage of one methyl group, i.e. benzyl ion **a** and CH_3 radical, or from **3a** ions, i.e. tolyl ions **c** and CH_3 radical, respectively, but is only slightly smaller than the potential energy of the reaction products from **2a** ions, i.e. tropylium ion **b** and CH_3 radical. Hence, isomerizations $[\mathbf{1a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ *and* $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ are predicted by the potential energy diagram in Scheme 1. Note that the energy barrier for the isomerization $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ is actually

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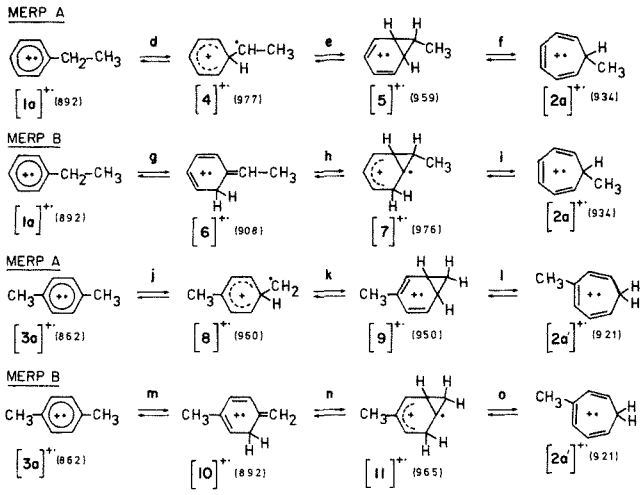


Scheme 1. *Reaction path* (MERP A and MERP B) for the interconversion of ions **1a**, **2a** and **3a**.

somewhat smaller than for $[\mathbf{1a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$, due to the stabilizing effect of the additional methyl group at the cyclic system.

To obtain a *dynamic* model of the reaction system the rates of the isomerization steps and of the fragmentations have been calculated according to the Ramsperger-Rice-Kassel-Marcus (RRKM) theory.[10] This allows one to follow the fate of $[C_8H_{10}]^{+\cdot}$ ions formed with a certain energy during the ionization process.[7] The following conclusions have been drawn from the dynamic model.

(1) The direct loss of a methyl group from either **1a** or **3a** ions is too slow to compete with the isomerization $[\mathbf{1a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ and $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$, respectively, even in molecular ions of high internal energy. As expected, **1a** and **3a** ions prefer to react by isomerization to **2a** ions and subsequent fragmentation to tropylium ions **b** and CH_3. This is true particularly for metastable ions of low potential energy.

(2) At a given potential energy of $[C_8H_{10}]^{+\cdot}$ the rate of isomerization of a 7-methylcycloheptatriene ion **2a** to an ethylbenzene ion **1a** and especially to a *p*-xylene ion **3a** is much faster than the reversed isomerization reactions. The wells for **1a** and **3a** ions on the potential energy surface are much deeper than for **2a** ions because of the greater thermodynamic stabilities of the former ions, and consequently for $[C_8H_{10}]^{+\cdot}$ ions of sufficient energy to cross the energy barriers for the isomerization, the density of states at the configuration of **1a** and **3a** will be always much higher than at the configuration of **2a**. This will slow down the rate of isomerization of $[C_8H_{10}]^{+\cdot}$ ions of structures **1a** and **3a**, compared with **2a** ions of the same potential energy. This 'depth of the well' effect, which is especially large for **3a** ions, explains the large kinetic shifts of the ionization energies of tropylium ions **b** from **1a**

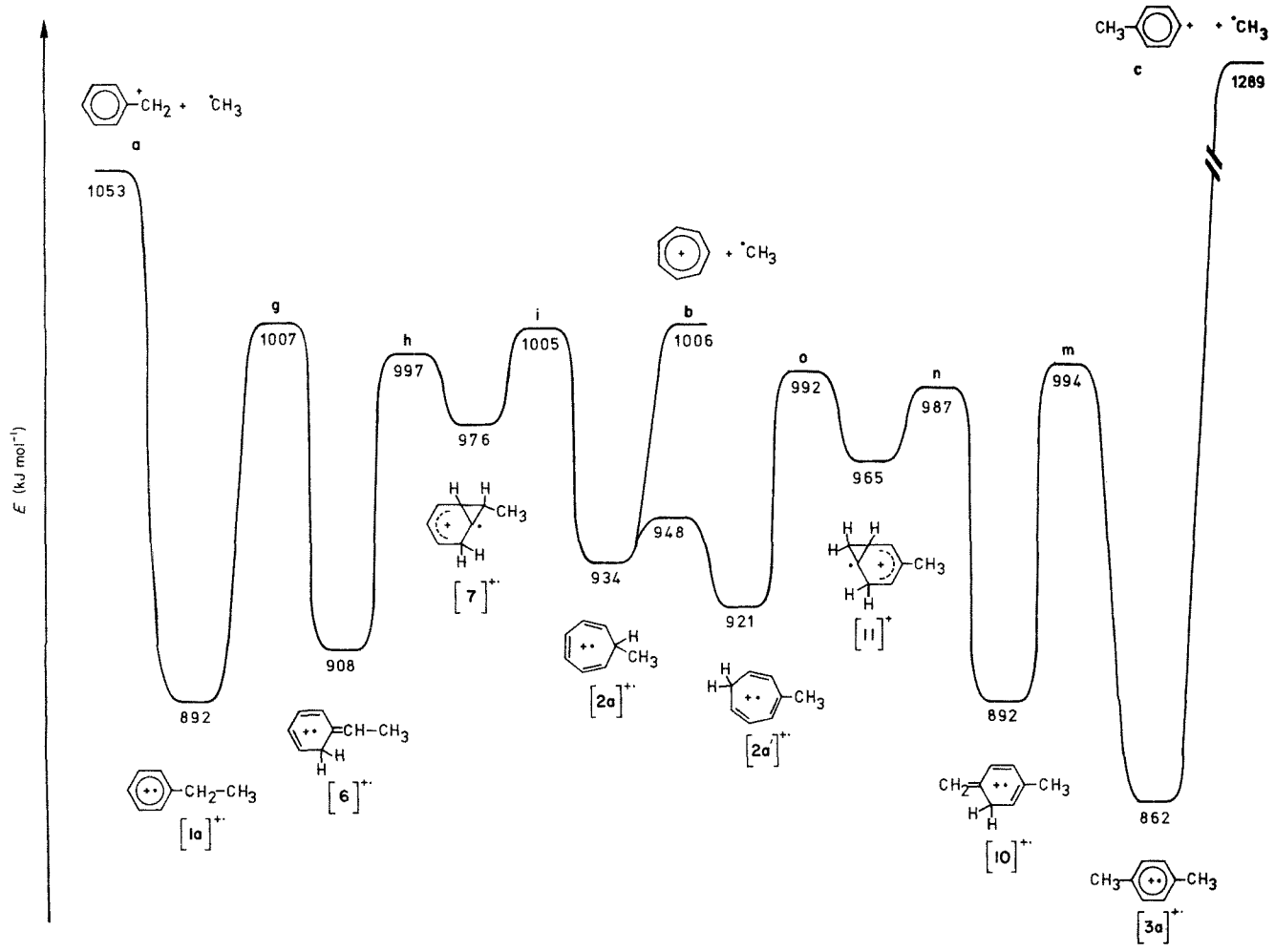


Figure 1. Potential energy profile for the interconversion and fragmentation of ions **1a**, **2a** and **3a** via MERP B.

Table 1. Calculated rate constants for the competing reactions of $[C_8H_{10}]^{+\cdot}$ ions with a potential energy of 1050 kJ mol^{-1} (metastable 1a and 3a ions)

Reaction	Rate constant (s^{-1})
$[\mathbf{1a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$	1×10^5
$[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$	1×10^5
$[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{1a}]^{+\cdot}$	1.5×10^8
$[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{3a}]^{+\cdot}$	3×10^9
$[\mathbf{2a}]^{+\cdot} \rightarrow \mathbf{b}+CH_3$	2×10^8

and **3a** and also the somewhat larger kinetic energy release during the fragmentation of **3a** ions.[6,7]

(3) Ions **2a** formed by isomerization from **1a** and **3a** ions are chemically activated species. Table 1 shows the rates calculated for the competing further reactions of these chemically activated species formed by isomerization in the metastable time-frame.[7] The isomerization of these activated **2a** ions to **3a** ions occurs with the greatest rate by far, while isomerization to **1a** ions and fragmentation to (**b**+$CH_3^{\cdot}$) have similar rates. Thus, the dynamic model predicts 'complete' isomerization between **2a** and **3a** ions if one starts with **3a** ions, but entering the $[C_8H_{10}]^{+\cdot}$ system at the side of **1a** most of the original **1a** ions will escape to **3a** ions after an initial rearrangement to ions of structure **2a** and before fragmentation.

(4) Metastable **2a** ions formed by electron impact ionization of **2a** are of less potential energy than the chemically activated **2a** ions formed by isomerization. The calculated rates[7] for the competing reactions of the 'true' metastable **2a** ions are shown in Table 2. Isomerization of these low energy **2a** ions to **3a** ions competes effectively with 'metastable fragmentation,' but the **3a** (and **1a**) ions thus formed will not react further within the reaction times accessible in a mass spectrometer. Hence, the rearranged 'metastable' **2a** ions are kinetically trapped as 'stable' **3a** and **1a** ions, respectively.

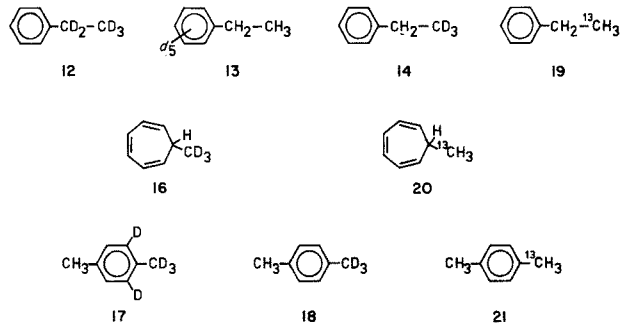
The predictions of the dynamic model of interconverting and fragmenting $[C_8H_{10}]^{+\cdot}$ ions have consequences with respect to the label distribution in fragmenting **1a**, **2a** and **3a** ions, respectively, specifically labelled with D or ^{13}C. The results of a study of deuterated compounds have been discussed previously.[7] As H/D migrations in the molecular ions without skeletal rearrangement may mimic or mask the effects of the skeletal isomerizations between **1a**, **2a** and **3a**, the fragmentations of $[C_8H_{10}]^{+\cdot}$ ions labelled with ^{13}C have been studied, repeating and extending earlier studies.[4,5]

Table 2. Calculated rate constants for the competing reactions of $[C_8H_{10}]^{+\cdot}$ ions with a potential energy of 1010 kJ mol^{-1} (metastable 2a ions)

Reaction	Rate constant (s^{-1})
$[\mathbf{2a}]^{+\cdot} \rightarrow \mathbf{b}+CH_3$	1×10^5
$[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{1a}]^{+\cdot}$	1.5×10^6
$[\mathbf{2a}] \rightarrow [\mathbf{3a}]^{+\cdot}$	3×10^7
$[\mathbf{1a}] \rightarrow [\mathbf{2a}]^{+\cdot}$	4×10^2
$[\mathbf{3a}] \rightarrow [\mathbf{2a}]^{+\cdot}$	2×10^2

RESULTS AND DISCUSSION

The ^{13}C labelled compounds and the D labelled derivatives discussed previously[7] are shown in Scheme 2. The results obtained for the loss of $^{12}CH_3$ and $^{13}CH_3$ from the molecular ions of ^{13}C labelled ethylbenzene (**19**), 7-methylcycloheptatriene (**20**) and *p*-xylene (**21**) in the ion source, the 1st field free region (FFR) and the 2nd FFR of a ZAB-2F mass spectrometer after electron impact (EI) ionization with 70 eV and 12 eV electrons, respectively, are shown in Table 3. The



Scheme 2. Labelled derivatives used for the investigations.

data for loss of $-CH_3$, $-CH_2D$, $-CHD_2$ and $-CD_3$ from the molecular ions of **12–18** at 70 eV under the same experimental conditions[7] are shown as bar diagrams for comparison in Fig. 2.

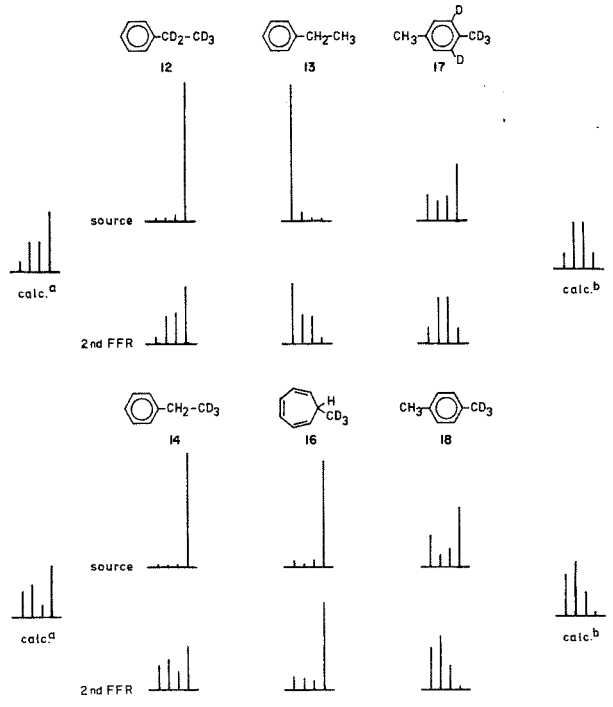


Figure 2. Label distribution for the loss of C(H, D)$_3$ from the deuterated derivatives **12–18**. The peak pattern shown represents (from the left to the right) loss of CH_3, CDH_2, CD_2H and CD_3 for decomposition in the ion source (upper line) and 2nd FFR (lower line), respectively.

(a) Calculated for 60% of a 'statistical' process and 40% of a 'specific' process.

(b) Calculated for a statistical label distribution.

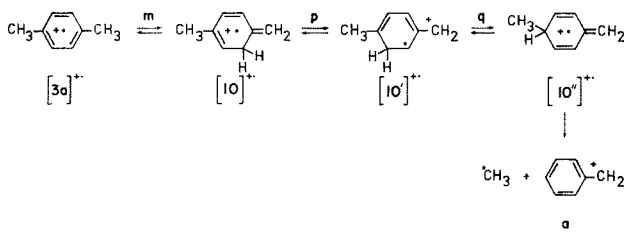
Table 3. Loss of (^{12}C, ^{13}C)H_3 from ^{13}C labelled derivatives 19 and 20

		19		20		21	
		70 eV	12 eV	70 eV	12 eV	70 eV	12 eV
Ion source	$^{12}CH_3$	9.3	10.5	9.6	12.6	48.7	49.9
	$^{13}CH_3$	90.7	89.5	90.4	87.4	51.3	50.1
1st FFR	$^{12}CH_3$	28.7	21.7	16.1	17.4	67.8	66.0
	$^{13}CH_3$	71.9	78.3	83.9	82.6	32.2	34.0
2nd FFR	$^{12}CH_3$	51.1	27.0	26.1	31.3	86.8	86.8
	$^{13}CH_3$	48.9	73.0	74.9	68.7	13.2	13.2

Xylene ions

The data for the formation of $[(^{12}C, ^{13}C)_7H_7]^+$ ions from **21** ions clearly show two mechanisms for the methyl loss. At both 70 eV and 12 eV the unstable xylene ions decompose in the ion source by losing equal amounts of $^{12}CH_3$ and $^{13}CH_3$. By contrast, at least 98% of metastable xylene ions decomposing in the 2nd FFR lose a methyl radical after a complete scrambling of all C atoms which corresponds to 12.5% loss of $^{13}CH_3$ and 87.5% loss of $^{12}CH_3$. The data observed for decomposition in the 1st FFR can be reproduced by assuming that 47.5% (70 eV) and 42.5% (12 eV), respectively, of the xylene ions fragment after scrambling of all C atoms, the remaining ions losing $^{12}CH_3$ and $^{13}CH_3$ in a 1:1 ratio.

The variation in the amounts of both competing reactions with reaction time and ion energy indicates that the loss of a methyl radical with a statistical distribution of the ^{13}C label over the reaction products must be a rather slow process with a low activation energy, which cannot compete for a fragmentation in the ion source, but dominates strongly in the metastable time-frame. The same result, i.e. complete scrambling of the label before loss of a methyl group, has been observed for the fragmentations of metastable **17** and **18** ions in the 2nd FFR (see Fig. 2). The present result clearly shows that this 'statistical' process corresponds to a scrambling by skeletal rearrangements and not only by hydrogen migrations. This is in agreement with the dynamic model for the isomerization and fragmentation of $[C_8H_{10}]^{+\cdot}$ ions, which predicts an equilibrium between methylcycloheptatriene ions **2a** and xylene ions **3a** (see Scheme 1) resulting in a scrambling of all C atoms and H atoms. (It should be noted that scrambling of C and H atoms is also possible by the route $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{10}]^{+\cdot} \rightarrow [\mathbf{11}]^{+\cdot} \rightarrow [\mathbf{11'}]^{+\cdot} \rightarrow [\mathbf{10^*}]^{+\cdot} \rightarrow [\mathbf{3a'}]^{+\cdot}$ if the intermediate ion $[\mathbf{11}]^{+\cdot}$ isomerises to its valence tautomer $[\mathbf{11'}]^{+\cdot}$.)



The 1:1 ratio for loss of $^{12}CH_3$ and $^{13}CH_3$ from unstable **21** ions in the ion source can be accounted for by loss of one of the original methyl substituents with equal probability. Although this 'specific' process has a higher activation energy, it must nevertheless be a very fast process because no competition by the statistical process is observed in the ion source. This is in conflict with the explanation of the specific loss of a methyl substituent by a direct bond cleavage and the formation of tolyl ions **c**. Although tolyl ions have been observed in the gas phase as stable species,[11] the calculated rates[7] show that the fragmentation $[\mathbf{3a}]^{+\cdot} \rightarrow \mathbf{c} + CH_3$ cannot compete with the isomerization $[\mathbf{3a}]^{+\cdot} \rightleftarrows [\mathbf{2a}]^{+\cdot}$ because of a very high activation energy. Additional information about the mechanism of the specific methyl loss is obtained from the peak pattern of $C(H, D)_3$ loss from the unstable **17** and **18** ions in the ion source. First, Fig. 2 shows that at 70 eV loss of an intact methyl substituent (CH_3 and CD_3, respectively) without any H and D migrations is the preferred, but by no means the only fragmentation. The peaks for loss of $-CH_2D$ and $-CHD_2$ indicate that 25–35% of the *p*-xylene ions lose a methyl substituent after exchange of one or two of its H(D) atoms. Since no interchange of the methyl-C and ring-C atoms is observed for this process in **21** ions, the exchange of H(D) atoms at the methyl groups and at the aromatic ring occurs independently of and faster than exchange of the respective C atoms by skeletal rearrangements. This corroborates well the exchange reactions observed in toluene ions.[12] Second, loss of CD_3 from the deuterated ions **17** and **18** exceeds that of CH_3 by a factor of 2.0 ± 0.2 and 2.4 ± 0.1 at 70 eV and 12 eV, respectively,[7] whereas **21** ions lose $^{12}CH_3$ and $^{13}CH_3$ in equal amounts. The large inverse D isotope effects observed for **17** and **18** reveal that the rate-determining reaction step during the loss of a methyl substituent from *p*-xylene ions involves a hydrogen migration.[13] The hydrogen exchange prior to loss of a methyl substituent and the large inverse D isotope effect are both explained by the well known 'H ring-walk' mechanism[9b,12] shown in Scheme 2. The MERP of this multi-step fragmentation as calculated by the MNDO method is shown in Fig. 3. The cleavage of the C—C bond in ions of structure **10''** has the highest activation energy in the reaction sequence. Note that benzyl ions **a** and not tolyl ions **c** are formed from *p*-xylene ions **3a** by this mechanism. The branching of the reactions leading to benzyl ions **a** and tropylium ions **b** from **3a** ions occurs at the stage of the methylencyclohexadiene ion **10**. Comparing the corresponding MERPs in Fig. 1 and Fig. 3 shows clearly that formation of ions **a** and the accompanying scrambling of hydrogen atoms independently of scrambling of the carbon atoms $[\mathbf{3a}]^{+\cdot} \rightleftarrows$

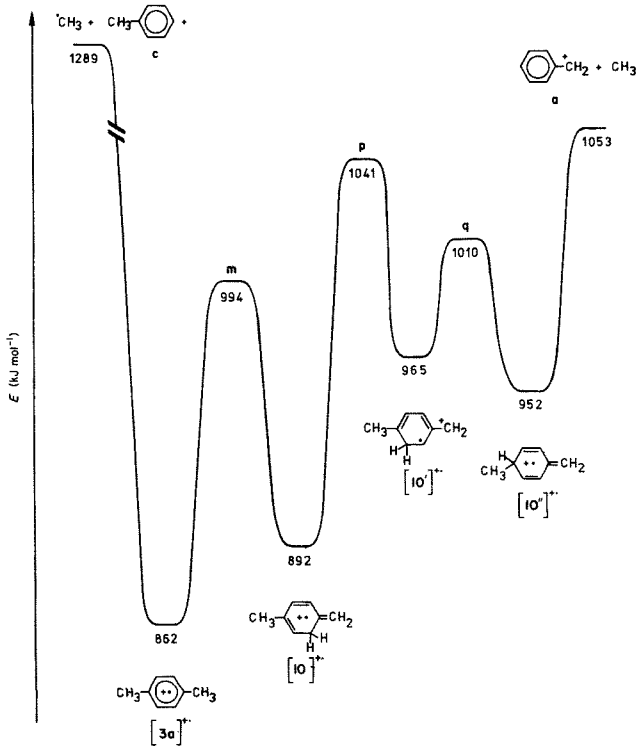


Figure 3. Potential energy profile for H migration and specific loss of a methyl substituent from **3a** ions.

$[\mathbf{10}]^{+\cdot} \rightleftarrows [\mathbf{10'}]^{+\cdot} \rightleftarrows [\mathbf{10''}]^{+\cdot}$ are high energy reactions, which should be observed only for **3a** ions decomposing in the ion source.

The rate of the formation of benzyl ions **a** from *p*-xylene ions **3a** has been calculated by the RRKM procedure, as discussed previously.[7] In Fig. 4 the curve

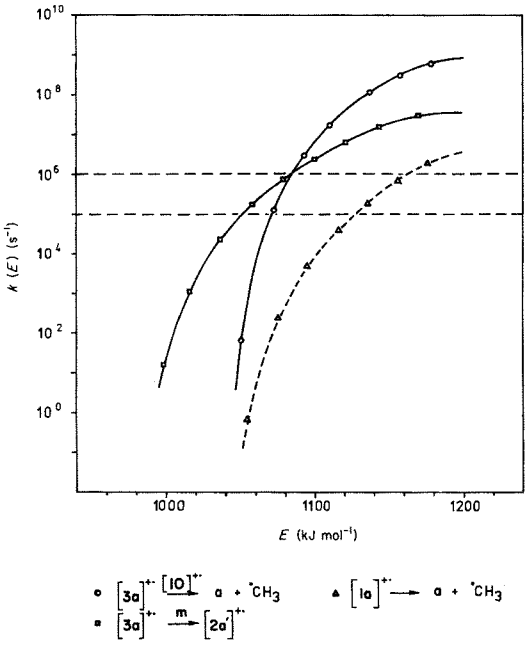


Figure 4. Calculated rate constants $k(E)$ vs potential energy for the reactions $[\mathbf{3a}]^{+\cdot} \rightarrow \mathbf{a} + CH_3$, $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ and $[\mathbf{1a}]^{+\cdot} \rightarrow \mathbf{a} + CH_3$.

for $k(E)$ vs potential energy is compared with corresponding rate curves of the competing skeletal rearrangement $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ and of the process $[\mathbf{1a}]^{+\cdot} \rightarrow \mathbf{a} + {}^{\cdot}CH_3$. The rate curve of the fragmentation $[\mathbf{3a}]^{+\cdot} \rightarrow \mathbf{a} + {}^{\cdot}CH_3$ by hydrogen rearrangement and specific loss of a methyl substituent (see Scheme 3) rises much more steeply with the potential energy of the system than the other two. The calculated rate curves for the processes $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$ and $[\mathbf{3a}]^{+\cdot} \rightarrow \mathbf{a} + {}^{\cdot}CH_3$ cross at potential energies of $[C_8H_{10}]^{+\cdot}$ ions near the upper limit for metastable **3a** ions. As a consequence, only a few percent of **3a** ions of larger potential energies rearrange to methylcycloheptatriene ions **2a** in the ion source and most of them decompose by specific loss of a methyl substituent, as required by the experimental results.

Ethylbenzene ions

It was concluded[7] from the results of the study of deuterium labelled ethylbenzenes **12–15** that a substantial number of ethylbenzene ions **1a** explore the region of xylene ions **2a** before loss of a methyl radical. This follows from the peak pattern for loss of $C(H, D)_3$ from **12–14** shown in Fig. 2 for the fragmentation in the ion source, and 2nd FFR after ionization at 70 eV, respectively, which *cannot* be reproduced by a calculation using a single exchange mechanism for the H(D) atoms approaching a statistical label distribution with increasing reaction time. However, fair agreement between experimental and calculated peak patterns is obtained by using two mechanisms for the loss of a methyl radical. The first corresponds to specific loss of the terminal methyl group from the side chain which can occur either by direct C—C bond cleavage in **1a** ions or by loss of this methyl group after a rearrangement to methylcycloheptatriene ions **2a**. As can be seen from the rate constants given in Table 1 the latter process is much more likely. The second mechanism involves complete scrambling of all H(D) atoms prior to loss of a $C(H, D)_3$ radical and increase with increasing ion lifetime. It has been suggested[7] that scrambling occurs by a rearrangement of **1a** ions to **3a** ions via **2a** ions, establishing an equilibrium between **2a** and **3a** ions for those **1a** ions which escape to the region $[\mathbf{3a}]^{+\cdot}$ of the $[C_8H_{10}]^{+\cdot}$ ion hypersurface before fragmentation.

The data from the present ^{13}C labelling study in Table 3 show that an increasing amount of $^{12}CH_3$ is lost from **19** ions with increasing lifetime, but a statistical label distribution is not reached even in the 2nd FFR. In Table 4 the relative amounts of the process for specific loss of the terminal methyl group and for statistical loss of the labels with the methyl radical calculated from the ^{13}C derivative **19** and the mean values calculated from the D derivatives **12–14** are compared. A good agreement between these values for the series at 70 eV and a fair one for the series at 12 eV is observed. Note that the exchange between H(D) atoms at the benzylic position and at the ring position, as discussed in the case of xylene ions, will not interfere with loss of the terminal methyl group. The good agreement between the relative amounts of

the specific process and the statistical one calculated from ^{13}C and D labelled derivatives proves that the statistical label distribution in the case of the deuterated compounds is not due to hydrogen migrations but is a consequence of deep-seated skeletal rearrangements of the ethylbenzene ions **1a** before formation of the $[C_7H_7]^+$ ion. Again this is in good agreement with the prediction of the dynamic model.

Interestingly, the data of Table 4 both for D and ^{13}C labelled ethylbenzenes show a *decrease* of fragmentation by the statistical process with a *decrease* in the energy of the ionizing electron beam. This effect is seen most clearly for fragmentations in the 2nd FFR and in this case is certainly larger than the experimental error. Two explanations can be given by the dynamic model for this effect. (1) The branching of chemically activated methylcycloheptatriene ions **2a** formed by rearrangement from ethylbenzene ions **1a** between fragmentation $[\mathbf{2a}]^{+\cdot} \rightarrow \mathbf{b} + CH_3$ and further rearrangement to xylene ions **3a** ($[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{3a}]^{+\cdot}$) increases with the energy of **2a** ions in favour of the isomerization $[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{3a}]^{+\cdot}$. (2) Lowering the electron energy from 70 eV to 12 eV increases (after rearrangement $[\mathbf{1a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$) the relative number of **2a** ions with a small amount of excess energy, which can still react further by the competing processes $[\mathbf{2a}]^{+\cdot} \rightarrow \mathbf{b} + CH_3$ and $[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{3a}]^{+\cdot}$. However, the energy of the **3a** ions formed is so small that they will not isomerize back to **2a** ions within their lifetime in the mass spectrometer. This will increase the relative amount of $[C_8H_{10}]^{+\cdot}$ ions fragmenting by the more direct route $[\mathbf{1a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot} \rightarrow \mathbf{b} + CH_3$ without scrambling of all C atoms. Because of the simplifications necessary for the calculations of the MERP and the rate curves of the competing processes[7] it is not possible to distinguish clearly between these explanations, but the 'kinetic trapping' of **2a** ions of small excess energy is more likely to be the reason for the observed decrease in the statistical process with decreasing electron energy.

Methylcycloheptatriene ions

The differences in the label distribution between the products of fragmenting unstable and metastable methylcycloheptatriene ions **2a** and xylene ions **3a**, respectively, has been the most serious argument against the interconversion of **2a** and **3a** ions.[6] However, as discussed previously,[7] it must be realized that one is sampling different species of **2a** ions by observing the loss of CH_3 from (originally) **2a** and **3a** ions at the reaction time of metastable ions. In the latter case chemically activated **2a** ions with a considerable amount of excess energy are formed by rearrangement of **3a** ions and they are 'metastable' only because of the slow rearrangement step $[\mathbf{3a}]^{+\cdot} \rightarrow [\mathbf{2a}]^{+\cdot}$. The rate data of Table 1 show that for $[C_8H_{10}]^{+\cdot}$ ions of this potential energy the equilibrium $[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{3a}]^{+\cdot}$ is possible. The 'true' metastable **2a** ions formed by electron impact from **2a** ions contain less excess energy. The rate constants in Table 2 for the reactions of **2a** ions of this energy show that the rearrangement $[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{3a}]^{+\cdot}$ still competes with the fragmentation $[\mathbf{2a}]^{+\cdot} \rightarrow \mathbf{b} + CH_3$, but that the back reaction of **3a** ions is several orders of magnitude too slow to occur within the lifetime of the ions in the mass spectrometer. Hence, the equilibrium of the ions $[\mathbf{2a}]^{+\cdot} \rightarrow [\mathbf{3a}]^{+\cdot}$ is not established for C_8H_{10} ions of this energy but the rearranged **2a** ions are trapped as stable **3a** ions. As a consequence of this 'kinetic trapping' most of the $[C_7H_7]^+$ ions are formed from metastable **2a** ions without a preceding skeletal rearrangement. This conclusion from the dynamic model of the interconversion of $[C_8H_{10}]^{+\cdot}$ ions is borne out by the experiments with the trideuteromethyl derivative **16**[7] and is also corroborated by the results obtained with the ^{13}C labelled compound **20** (see Table 5).

In the ion source 87±2% of **20** ions fragment by a specific loss of the $^{13}CH_3$ substituent without skeletal rearrangement. The value of 83±3% calculated for a specific loss of the intact CD_3 group from **16** ions is somewhat smaller, probably because of a mixing of the H(D) atoms at the different positions by H(D) migrations independently of a skeletal rearrangement. The relative amount of this 'specific' methyl loss decreases gradually to 67±3% (**20**) and 69±3% (**16**) for metastable ions reacting in the 2nd FFR.

Table 4. Relative contributions of the 'statistical' process to the fragmentation of ethylbenzene ions

	^{13}C label (19)		D label (12–14)	
	70 eV	12 eV	70 eV	12 eV
Ion source	11%	12%	10±3%	10±3%
1st FFR	32%	25%	32±5%	20±3%
2nd FFR	59%	31%	61±3%	36±7%

Table 5. Relative contributions of the 'statistical' process to the fragmentations of methylcycloheptatriene ions

	^{13}C label (20)		D label (16)	
	70 eV	12 eV	70 eV	12 eV
Ion source	11%	14%	14%	19%
1st FFR	18%	20%	15%	19%
2nd FFR	30%	35%	30%	33%

CONCLUSION

The results of this study of the fragmentation of ^{13}C labelled molecular ions of ethylbenzene, methylcycloheptatriene and *p*-xylene in the ion source and in the 1st FFR and 2nd FFR, respectively, of a VG ZAB-2F mass spectrometer are in good agreement with D labelling studies. This shows clearly that the label distribution between the reaction products $[C_7H_7]^+$ ion and CH_3 radical observed at long reaction times is due to skeletal rearrangements of the molecular ions. Qualitatively, the results can be understood by a dynamic model for the interconversion and fragmentation of $[C_8H_{10}]^{+\cdot}$ ions which take into account the

potential energy diagram *and* the rates for the competing reactions of these ions.

A comparison of the fragmentations of deuterated and ^{13}C labelled *p*-xylene ions shows that high energy ions fragmenting in the ion source react by hydrogen migrations independently of skeletal rearrangement and specific loss of a methyl substituent. These fast reactions can be explained by a 'ring walk' mechanism.

EXPERIMENTAL

The mass spectra were measured with a VG ZAB 2F double focusing instrument with reversed geometry under the following conditions: electron energy 70 eV and 12 eV, emission current 50 μA, accelerating voltage 6 kV, source temperature *c.* 200 °C. The samples were introduced by the septum-inlet system. The mass spectra represent the average of two sets of at least six scans taken on two different days. The metastable ion spectra were obtained by linked scan and MIKE spectroscopy for the 1st and 2nd FFR, respectively. The preparation of the deuterated compounds has been described elsewhere.[7] The physical constants of the ^{13}C labelled compounds are equal to the unlabelled ones given in the literature. The labelling purity of each compound was examined by mass spectrometry at 12 eV electron energy.

[α-^{13}C]Ethylbenzene (19)

[α-^{13}C]Ethylbenzene was obtained by a Grignard reaction of benzaldehyde with [^{13}C]methylmagnesiumiodide. The resulting alcohol was reduced by catalytic hydration with Pd/C and H_2. Yield 88%. Isotopic purity ^{13}C 92%, ^{12}C 8%.

[7-^{13}C]Methylcycloheptatriene (20)

[7-^{13}C]Methylcycloheptatriene was synthesized by reaction of [^{13}C]methylmagnesium iodide with 7-methoxycycloheptatriene.[14] Yield 78%. Isotopic purity ^{13}C 93%, ^{12}C 7%.

[1-^{13}C]Methyl-4-methylbenzene (21)

[1-^{13}C]Methyl-4-methylbenzene was obtained by coupling [^{13}C]methylmagnesiumiodide to 1-bromo-4-methylbenzene according to a procedure given by Kumada *et al.*[15] Yield 86%. Isotopic purity ^{13}C 95%, ^{13}C 5%.

The calculations were carried out by the standard MNDO[8] procedure. The RRKM calculation were carried out by the RRKM program[10b] with the direct count option. The performance of both calculations has been described elsewhere.[7]

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REFERENCES

1. Mechanisms of mass spectrometric fragmentation reactions—XXXIV. Part XXXIII: J. Grotemeyer and H.-Fr. Grützmacher, in *Current Topics in Mass Spectrometry and Chemical Kinetics*, ed. by A. Maccoll, pp. 29–59. Heyden, London (1982).
2. For details see: (a) R. A. W. Johnstone (Ed.), *Mass Spectrometry*, Specialist Periodical Report Vol. 4, p. 38ff. The Chemical Society, London (1977); (b) K. Levsen, in *Fundamental Aspects of Organic Mass Spectrometry*, Vol. 4, *Progress in Mass Spectrometry*, ed. by H. Budzikiewicz, Chapt. V. Verlag Chemie, Weinheim (1978).
3. P. N. Rylander, S. Meyerson and H. M. Grubb, *J. Am. Chem. Soc.* **79**, 842 (1957).
4. F. W. McLafferty and J. Winkler, *J. Am. Chem. Soc.* **96**, 5182 (1974).
5. (a) A. Venema, N. M. M. Nibbering and Th. J. De Boer, *Tetrahedron Lett.* 2141 (1971); (b) A. Venema, Academic Proefschrift, University of Amsterdam (1975).
6. B. J. Stapleton, R. D. Bowen and D. H. Williams, *J. Chem. Soc., Perkin Trans. 2* 1219 (1979).
7. J. Grotemeyer and H.-Fr. Grützmacher, *Current Topics in Mass Spectrometry and Chemical Kinetics*, ed. by A. Maccoll, pp. 29–59. Heyden, London (1982).
8. MNDO: W. Thiel, *QCPE* **4**, 379 (1979).
9. (a) C. Cone, M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.* **99**, 372 (1977); (b) M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.* **99**, 2446 (1977).
10. (a) IE: J. Robinson and K. A. Holbrook, *Unimolecular Reactions*, Wiley, New York (1972); (b) RRKM: W. L. Hase and D. L. Buenker, *QCPE* **9**, 234 (1973).
11. F. W. McLafferty and F. M. Bockhoff, *Org. Mass Spectrom.* **14**, 181 (1979).
12. M. A. Baldwin, F. W. McLafferty and D. M. Jerina, *J. Am. Chem. Soc.* **97**, 6169 (1975).
13. H. Schwarz, *Org. Mass Spectrom.* **15**, 491 (1980).
14. J. Couzow, *J. Am. Chem. Soc.* **83**, 2343 (1961).
15. K. Tamao, K. Samitari and M. Kumada, *J. Am. Chem. Soc.* **94**, 4374 (1972).

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