Kinetic Energy Release as a Probe for Rate-determining Unimolecular Isomerisations. Energetics of Ring Expansion in Ionised Halogenobenzenes and Alkylbenzenes

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The mechanism whereby radical loss occurs from the molecular ions of numerous halogeno-aromatic and alkyl-aromatic compounds is investigated using the kinetic energy release which accompanies dissociation, the non-occurrence of plausible competing reactions, and appearance potential measurements. Slow elimination of a bromine radical from ionised bromobenzene is formulated as a simple cleavage and is evidenced by little kinetic energy release. In contrast, the major slow dissociations (metastable transitions) of ionised halogenotoluenes (halogen radical loss), xylenes and polymethylbenzenes (methyl radical loss), and toluene (hydrogen radical loss) all occur after ring expansion to ionised cycloheptatriene isomers. In these cases (apart from ionised toluene and ethylbenzene) the ring expansion process is rate-determining and the subsequent fast decompositions give rise to relatively large releases of kinetic energy. Further support for the analysis may be found from earlier work on these systems involving ^{2}H- and ^{13}C-labelling experiments; in particular, the observation of an isotope effect associated with the ring expansion of ionised *p*-chloroethylbenzene is strong evidence that this is the rate-determining step for $Cl^\cdot$ loss.

THE slow unimolecular reactions of organic ions in the gas phase may be studied conveniently by means of conventional double-focusing mass spectrometers.[1] The decomposition of metastable ions in the field-free regions of such instruments occurs after a well defined time (usually *ca.* 10^{-5} s) thus permitting many vibrations (roughly 10^8) to take place prior to dissociation. As a direct consequence there is, to a good approximation, enough time for each ion to sample essentially all energetically accessible reactant configurations. It follows that the ability of the various decay routes to compete with one another depends mainly upon the relative activation energies of the processes concerned.[2]

The excess energies present in the transition states when metastable ions decompose are usually small [3] and comparable to those found in solution experiments. However, information concerning the kinetic energy released upon decomposition is only available from gas-phase methods because of the effects of collisions which are inevitable in solution. These additional data, which may be readily obtained from a consideration of the metastable peak for dissociation, are often extremely useful.[4] For example, when a narrow peak is observed, thus indicating little kinetic energy release, it may be concluded that there is at most a small translational component to any reverse activation energy. Indeed, this peak shape is consistent with (but does not prove that) decomposition occurs with a negligible reverse activation energy. Thus, for instance, direct cleavage reactions, such as radical losses, often give rise to narrow metastable peaks. In some cases broad peaks are observed; this reveals that a relatively large average [5] kinetic energy release accompanies dissociation. The most probable general cause for this phenomenon is the occurrence of rate-determining rearrangement of one structure to a second isomer prior to decomposition. Much greater excess energies are now present in the transition states for the final steps than is usually the case when metastable ions decompose. Part of these excess energies may be partitioned as translation; therefore larger average kinetic energy releases may be observed.[6]

A problem which has attracted considerable attention in organic mass spectrometry is the possibility of isomerisation or equilibration of ionised toluene and cycloheptatriene derivatives.[7] In the case of the parent molecules, ionised toluene and cycloheptatriene, interconversion occurs rapidly prior to decomposition at energies appropriate to metastable transitions.[8-10] A recent theoretical analysis [11] resulted in a calculated energy barrier of 140 kJ mol^{-1} for rearrangement of ionised toluene to ionised cycloheptatriene. This is consistent with the experimental facts which require this energy barrier to be less than that (190 kJ mol^{-1}) needed to cause hydrogen radical loss from the molecular ion of toluene. It is feasible that in homologous systems, new decomposition pathways might become available which require less energy than ring expansion (or ring contraction). If this situation were to be realised, interconversion of the ionised toluene and cycloheptatriene derivatives would be pre-empted and rate-determining rearrangements might be observed. It seems of interest to explore this possibility and, if suitable systems can be discovered, to obtain limits on the activation energy (or energies) for ring-expansion of aromatic radical cations. Two series of homologous ions are discussed in this paper; first the molecular ions of halogeno-aromatic species and secondly some representative ionised alkylaromatic compounds.

RESULTS AND DISCUSSION

Halogeno-aromatic Compounds.—Ionised bromobenzene eliminates a bromine radical in slow dissociations; this reaction gives rise to a narrow metastable peak [Figure 1(a); there are two peaks, each of which is narrow, owing to the occurrence of ^{79}Br and ^{81}Br in approximately equal abundance]. In view of the relatively small average [5] kinetic energy release of 6.9 kJ

mol^{-1}, it seems likely that this reaction is a simple bond cleavage leading to phenyl cation and a bromine radical. Similarly, loss of $Cl^{\bullet}$ and $I^{\bullet}$ from ionised chlorobenzene and iodobenzene may also be formulated as direct cleavages since relatively small average kinetic energy releases are associated with these reactions (Table 1).

In contrast to this behaviour, elimination of $Cl^{\bullet}$ and $Br^{\bullet}$ from ionised *p*-halogenotoluenes releases much more kinetic energy (Table 1). In the case of ionised *p*-bromotoluene this energy release is so large that the two metastable peaks, corresponding to loss of the two isotopes of bromine, are sufficiently broadened that they coalesce into an apparently single broad peak [Figure 1(b)]. Clearly, there is a fundamental difference between $Br^{\bullet}$ loss from ionised bromobenzene and bromotoluene, the latter reaction no longer proceeding *via* direct cleavage of the C–Br bond. Such a reaction would lead to the production of a methyl substituted phenyl cation; however, ring expansion followed by $Br^{\bullet}$ loss can result in the formation of the energetically more favourable cycloheptatriene cation (Scheme 1). This possibility is of course precluded for the lower homologue; hence, direct cleavage occurs.

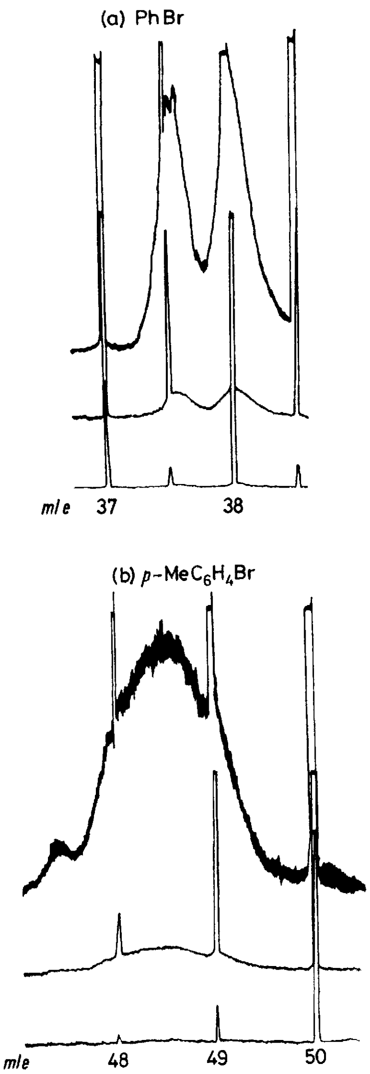
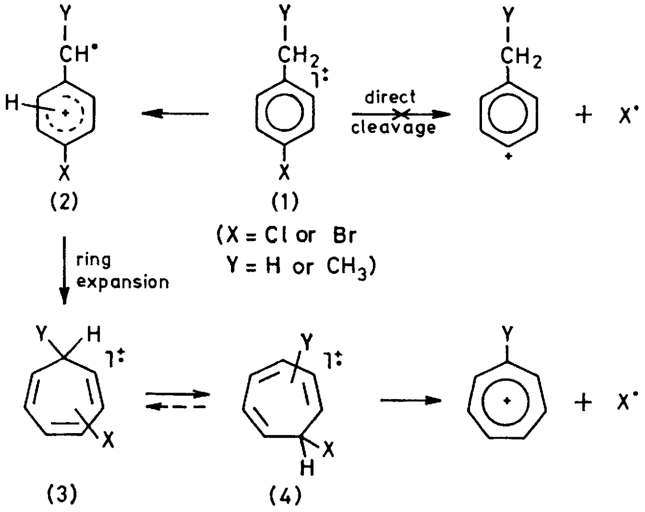


FIGURE 1 Second field-free region metastable peaks for bromine radical loss: (a) from ionised bromobenzene, and (b) from ionised *p*-bromotoluene



SCHEME 1

TABLE 1

Average[5] kinetic energy release associated with halogen radical loss from some ionised halogenoaromatic compounds

Precursor structure	Average kinetic energy release (in kJ mol^{-1}) accompanying halogen radical ($X^{\bullet}$) loss [a]		
	X = Cl	X = Br	X = I
PhX	7.4	6.9	5.6
p-MeC_6H_4X	11.8	26.5 [b]	*c*
$PhCH_2X$	5.7	1.4	1.9 [d]
p-EtC_6H_4X	15.0	21.7 [b]	*e*

[a] Measured from second field-free region metastable peaks. [b] Less accurate value owing to overlap of metastable peaks. [c] Composite metastable peak observed. [d] Measured from first field-free region metastable peak owing to low abundance of corresponding second field-free region metastable peak. [e] Data not available.

The precise nature of the mechanism whereby ring expansion of species with general formula (1) occurs is not known; however, it seems plausible that intermediates such as (2) are involved. Thus, hydrogen radical migration from benzylic position in (1) on to the aromatic ring produces (2); insertion of the carbon atom formally carrying the radical site may then occur between two carbon atoms in the aromatic nucleus. This insertion, which may proceed *via* bicyclic species (*e.g.* ionised norcaradiene derivatives), might occur between two specific ring carbon atoms, or, alternatively, might take place between any two adjacent ring carbon atoms. In any case, a species of general formula (3) would be formed; after a 1,2-hydride shift (or shifts), leading to the isomeric radical cation (4), $X^{\bullet}$ loss may occur with the formation of a substituted tropylium cation.

Regardless of the exact mechanism whereby (1) may isomerise to (4), it is clearly of interest to enquire how much energy is required to cause this rearrangement. The non-occurrence of simple cleavage in the elimination of $\mathrm{Br}^{\bullet}$ and $\mathrm{Cl}^{\bullet}$ from ionised *p*-bromotoluene and *p*-chlorotoluene, respectively, demonstrates that these processes have higher activation energies than the corresponding rearrangements. Relevant thermochemical data are given in Figure 2; where experimental values for heats of formation are not available, recourse has been made to estimates, made on a group equivalent basis,[12,13] based upon values for lower homologues.[13] Figure 2 shows the energy levels for $\mathrm{Br}^{\bullet}$ loss from ionised *p*-bromotoluene; a similar energy diagram may be constructed for the corresponding *p*-chlorotoluene system.

Direct cleavage of the C–Br bond in ionised *p*-bromotoluene would lead to products having a total heat of formation of *ca.* 1 270 kJ mol^{-1}; since this process is pre-empted by ring expansion, it follows that ring expansion must proceed *via* a transition state with an energy lower than 1 270 kJ mol^{-1}. Moreover, the non-occurrence of $\mathrm{H}^{\bullet}$ loss permits a still lower limit of 1 135 kJ mol^{-1} to be fixed for the maximum value of the heat of formation of this transition state. This corresponds to an upper limit of 235 kJ mol^{-1} for the activation energy for ring expansion of ionised *p*-bromotoluene. These arguments are based on the assumption that loss of $\mathrm{Br}^{\bullet}$ or $\mathrm{H}^{\bullet}$ from ionised *p*-bromotoluene would proceed without significant reverse activation energy. If a reverse activation energy were involved, the upper limits, deduced for the activation energy for ring expansion of ionised *p*-bromotoluene, would be increased.

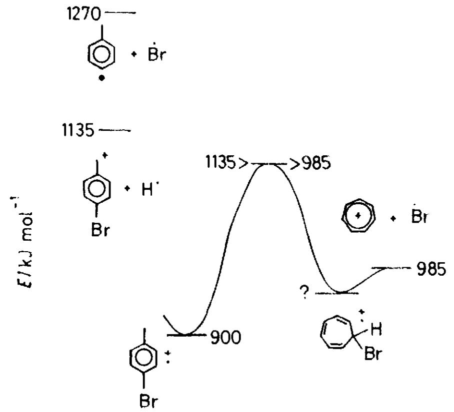


FIGURE 2 Potential energy profile for isomerisation and dissociation of ionised *p*-bromotoluene

Similarly, because the ring expansion process is the rate-determining step in $\mathrm{Br}^{\bullet}$ loss, it must involve a transition state of higher energy than the total heat of formation (985 kJ mol^{-1}) of the products. This allows a lower limit of 85 kJ mol^{-1} to be assigned for the activation energy for ring expansion of ionised *p*-bromotoluene. An analogous series of arguments for ionised *p*-chlorotoluene shows that the activation energy for ring expansion lies between 140 and 235 kJ mol^{-1} in this case.

Loss of $\mathrm{X}^{\bullet}$ from ionised benzyl halides occurs with only a small average kinetic energy release, thus suggesting direct cleavage occurs in these cases. The metastable peaks for X = Br and I are especially narrow, corresponding to average[5] kinetic energy releases of only 1.4 and 1.9 kJ mol^{-1}, respectively (Table 1). This result is hardly surprising in view of the stable product ion, benzyl cation, which is known from collisional activation studies[14,15] and ion cyclotron resonance experiments[16] to exist in a significant potential energy well.

The relatively large average kinetic energy release which accompanies $\mathrm{X}^{\bullet}$ loss from ionised *p*-halogenoethylbenzenes (X = Cl or Br, Table 1) reveals that these reactions occur *via* rate-determining rearrangement to ionised cycloheptatriene structures. Further evidence for this postulate stems from earlier deuterium labelling experiments[17] on these systems.

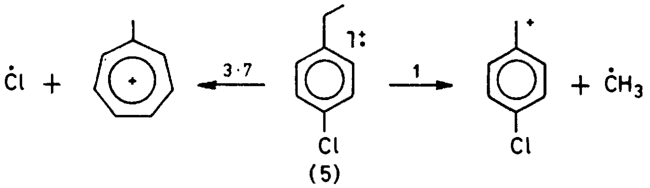
Two competing slow dissociations of (5) and (6) are observed, namely loss of a halogen radical and loss of a methyl radical. In each case, methyl radical loss is the minor process in the first field-free region, halogen radical loss being some four times more abundant.[17] However, if the hydrogen atoms in the benzylic positions of (5) and (6) are progressively replaced by deuterium, $^{\bullet}\mathrm{CH_3}$ loss increases in abundance relative to $\mathrm{Cl}^{\bullet}$ or $\mathrm{Br}^{\bullet}$ elimination (Table 2). The effect is quite marked and is consistent with a primary deuterium isotope effect operating in the rate-determining step for halogen radical loss but not methyl radical loss. Thus, it would appear probable that $^{\bullet}\mathrm{CH_3}$ loss from (5) and (6) occurs *via* direct cleavage, to form benzylic type ions, whereas

TABLE 2

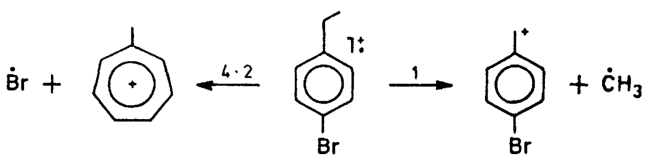
Observed channelling ratios for decomposition of ionised *p*-halogenoethylbenzenes

Compound	$\mathrm{X}^{\bullet}$ loss [a] / $^{\bullet}\mathrm{CH_3}$ loss
p-$\mathrm{ClC_6H_4 \cdot CH_2 \cdot CH_3}$	3.71 ± 0.20
p-$\mathrm{ClC_6H_4 \cdot CHD \cdot CH_3}$	1.83 ± 0.06
p-$\mathrm{ClC_6H_4 \cdot CD_2 \cdot CH_3}$	1.37 ± 0.05
p-$\mathrm{BrC_6H_4 \cdot CH_2 \cdot CH_3}$	4.23 ± 0.03
p-$\mathrm{BrC_6H_4 \cdot CD_2 \cdot CH_3}$	1.92 ± 0.02

[a] Measured for metastable ions dissociating in the first field-free region of an AEI MS 9 mass spectrometer; data taken from ref. 17.



(5)



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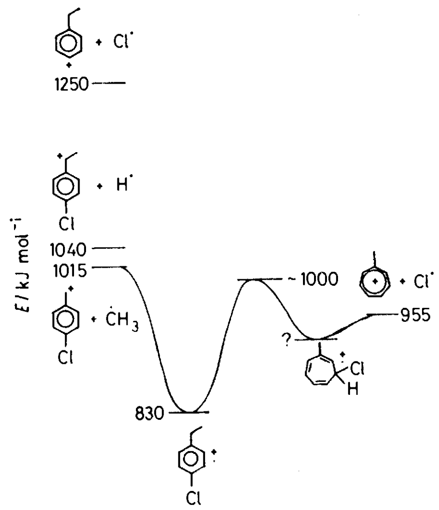


FIGURE 3 Potential energy profile for isomerisation and dissociation of ionised *p*-chloroethylbenzene

$\mathrm{X}^{\bullet}$ loss involves ring expansion leading to a methyltropylium cation.

The competition between these two decay routes ought to permit an accurate estimate to be made for the activation energy for ring expansion of ionised *p*-halogenoethylbenzenes. Relevant thermochemical data are given in Figure 3. The energy level diagram appropriate to ionised *p*-chloroethylbenzene is considered; a very similar diagram may be constructed for the corresponding bromo-aromatic system.

From Figure 3, it is evident that the activation energy required to cause ring expansion of ionised *p*-chloroethylbenzene must be *ca.* 170 kJ mol^{-1} (*i.e.* marginally less than that required to promote $^{\bullet}\mathrm{CH}_3$ loss *via* direct cleavage). This follows because $^{\bullet}\mathrm{CH}_3$ loss is the minor decay channel. Since the sum of the heats of formation of the tropylium ion and $\mathrm{Cl}^{\bullet}$ is 955 kJ mol^{-1}, there is excess energy in the transition state for the dissociation step (Figure 3), and the average kinetic energy release accompanying dissociation is relatively large (Table 1). It is instructive in this connection to consider the non-occurrence of $\mathrm{H}^{\bullet}$ loss, which would lead to products having a total heat of formation only 25 kJ mol^{-1} above that of the products of $^{\bullet}\mathrm{CH}_3$ loss. Thus, few ions which decompose in metastable transitions have sufficient internal energy to attain a transition state of energy 1 040 kJ mol^{-1}.

For the analogous ionised bromo-aromatic system, a similar argument results in an estimate of 170 kJ mol^{-1} for the activation energy for ring expansion. This value compares well with that derived in the chloro-aromatic case, although the errors inherent in the method may be as large as ± 40 kJ mol^{-1}.

A final point in connection with these ionised halogeno-aromatic systems is that direct fission of the ring-carbon to halogen bond would require some 180—250 kJ mol^{-1} more energy than ring expansion. Hence, direct cleavage is easily pre-empted by rate-determining ring expansion in these cases.

Alkyl-aromatic Compounds.—A considerable amount of research has been conducted into the isomerisation and dissociation of ionised toluene and related isomers.[7-10,14,15] There is overwhelming evidence[8-10] that interconversion of ionised toluene and cycloheptatriene occurs prior to slow decomposition to form $\mathrm{C}_7\mathrm{H}_7^+$ and $\mathrm{H}^{\bullet}$. Collisional activation studies[14,15] reveal that both ionised toluene and cycloheptatriene eliminate $\mathrm{H}^{\bullet}$ to form a mixture of tropylium and benzyl cations, with the former ion structure predominating. Relevant energetics are given in Figure 4 from which it is evident that the activation energy for ring expansion of ionised toluene must lie between 105 and 190 kJ mol^{-1}. The former figure refers to the difference in heat of formation of ionised toluene and cycloheptatriene; since there is considerable disagreement over the heat of formation of ionised cycloheptatriene derivatives,[11] this value may be relatively unreliable. A recent theoretical analysis[11] yielded a value of 140 kJ mol^{-1} for this activation energy; this lies near the middle of the range required by experiment.

Three possible cases may be considered for the next homologue, $\mathrm{C}_8\mathrm{H}_{10}^{+\bullet}$; these are ionised ethylbenzene, xylenes, and methylcycloheptatriene. In each case, loss of $^{\bullet}\mathrm{CH}_3$ occurs in high abundance in the slow dissociations of these ions; the average kinetic energy releases and measured transition state energies associated with these reactions are given in Table 3. These data suggest that ionised methylcycloheptatriene and ethylbenzene interconvert prior to dissociation; in contrast, the ionised xylene isomers do not interconvert with either of the other structures. The most likely explanation is that the ionised xylenes undergo rate-determining ring expansion, *via* intermediates of closely similar heats of formation or *via* a common intermediate, to form ionised methylcycloheptatriene which then eliminates $^{\bullet}\mathrm{CH}_3$ relatively rapidly. This is supported by the observation that $^{\bullet}\mathrm{CH}_3$ loss from the ionised xylenes always releases the same average kinetic energy (14.7 kJ mol^{-1}) which is some 25% greater than the corresponding value (11.6 kJ mol^{-1}) found for ionised ethylbenzene and methylcycloheptatriene. The differ-

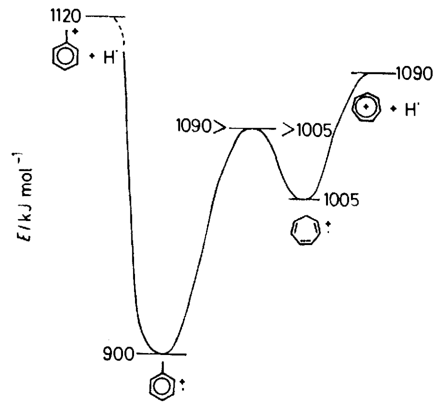


FIGURE 4 Potential energy profile for interconversion and dissociation of ionised toluene and cycloheptatriene

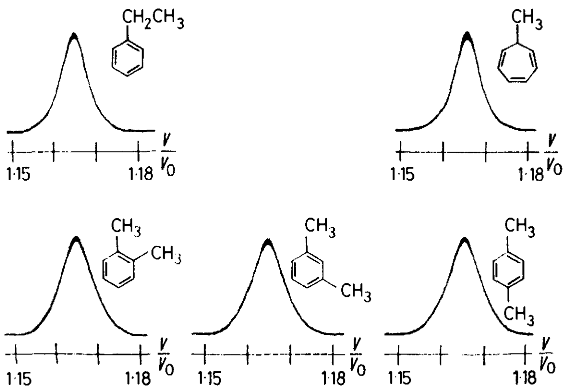


FIGURE 5 First field-free region metastable peaks for methyl radical loss from some isomers of $C_8H_{10}^{+\cdot}$; the abscissae are in units of V/V_0 where V_0 is the accelerating voltage used to transmit the main beam and V is the corresponding voltage required to transmit $C_7H_7^+$ ions formed in the first field-free region

ence in kinetic energy release is clearly visible from the shapes of the requisite metastable peaks; Figure 5 shows a set of such peaks, measured consecutively under identical instrumental conditions, for ions decomposing in the first field-free region.

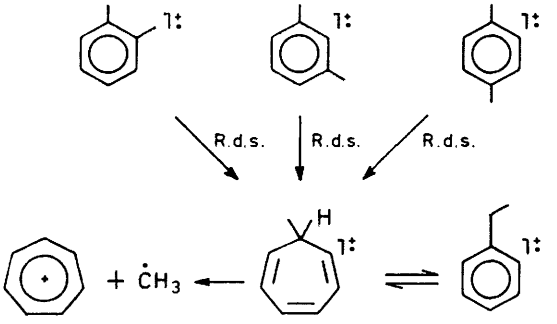
TABLE 3

Average kinetic energy releases and measured transition state energies associated with methyl radical loss from some isomers of $C_8H_{10}^{+\cdot}$

Precursor	Average [5] kinetic energy release [a] (kJ mol^{-1})	Measured transition state energy (kJ mol^{-1})
7-Methylcycloheptatriene	11.6	*b*
Ethylbenzene	11.6	1 050
o-Xylene	14.7	1 090
m-Xylene	14.7	1 095
p-Xylene	14.6	1 085

[a] Measured from second field-free region metastable peaks. [b] Data not available.

A plausible mechanism whereby $^{\cdot}CH_3$ loss may occur from these species is given in Scheme 2. Ionised xylene isomers undergo a rate-determining isomerisation, *via* transition states which have very similar energies (or *via* the same transition state) to ionised methylcycloheptatriene which then loses $^{\cdot}CH_3$ rapidly. Starting from ionised ethylbenzene or methylcycloheptatriene, elimination of $^{\cdot}CH_3$ requires more energy than interconversion; hence, these ions interconvert prior to dissociation. However, the energy needed to form any isomer of ionised xylene, presumably *via* ring contraction of ionised methylcycloheptatriene, is greater than that required to promote $^{\cdot}CH_3$ loss. Consequently, ionised methylcycloheptatriene loses $^{\cdot}CH_3$ in preference to isomerising to any ionised xylene. On the other hand, the lowest energy decay channel for any ionised xylene isomer is ring expansion to ionised methylcycloheptatriene. After this rate-determining rearrangement, relatively fast elimination of $^{\cdot}CH_3$ occurs, thus giving rise to broader metastable peaks than those observed starting from ionised methylcycloheptatriene or ethylbenzene.



SCHEME 2 R.d.s. = rate-determining step

The mechanism given in Scheme 2 requires that the original methyl group in ionised methylcycloheptatriene retains its identity and is eventually eliminated intact when dissociation takes place. This is consistent with earlier ^{2}H-labelling studies [18] which reveal that this methyl group retains its integrity to a considerable extent, even for ions of long lifetimes.

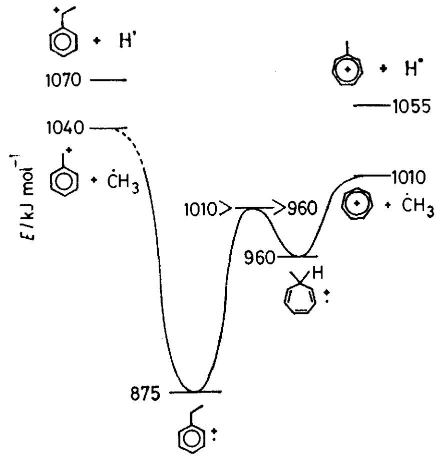


FIGURE 6 Potential energy profile for interconversion and dissociation of ionised ethylbenzene and methylcycloheptatriene

Relevant energetic data are given in Figures 6 and 7; reliable heats of formation are available from several sources,[13,19,20] and the value for ionised methylcycloheptatriene is estimated from that reported [13] for the lower homologue on the basis of a group equivalent method.[12,13]

Figure 6 shows the energy levels appropriate for $^{\cdot}CH_3$ loss from ionised ethylbenzene and methylcycloheptatriene. Since interconversion of these ions occurs prior to decomposition through the same transition states, it follows that the activation energy for ring expansion of ionised ethylbenzene must lie in the range 85—135 kJ mol^{-1}. The non-occurrence of H$^{\cdot}$ loss, which would lead to products with a total heat of formation of 60 kJ mol^{-1} above that for $^{\cdot}CH_3$ loss, may be explained because ring expansion followed by $^{\cdot}CH_3$ loss is energetically more favourable.

Figure 7 shows the analogous energy levels pertaining to dissociation and ring expansion of ionised xylene isomers. Rate-determining rearrangement of the ionised xylene isomers to ionised methylcycloheptatriene occurs; hence, the activation energy for ring expansion of the ionised xylenes must lie in the range 170—220 kJ mol^{-1}. The lower limit of this range corresponds to the energy needed to form tropylium cation and $^{\cdot}CH_3$ whilst the upper bound is derived from the energy required to promote $H^{\cdot}$ loss. The latter reaction is only a minor (*ca.* 2%) decay route of ionised xylenes; therefore it is likely that the energy required to cause ring expansion, and subsequent $^{\cdot}CH_3$ loss, is less than that needed to eliminate $H^{\cdot}$ either by direct cleavage of an ionised xylene or by decomposition of ionised methylcycloheptatriene. Loss of $^{\cdot}CH_3$ from ionised xylenes *via* direct cleavage, thus producing methylphenyl cations, would require a further 250 kJ mol^{-1} of internal energy and is therefore pre-empted by ring expansion which is energetically more favourable.

It is interesting to compare the activation energies required to cause ring expansion of ionised toluene, xylenes, and ethylbenzene. The ranges found for these processes are respectively 105—190, 170—220, and 85—135 kJ mol^{-1}. It appears that the energy needed to cause assimilation of a methyl group into an ionised aromatic ring is more than that required to promote conversion of an ethyl group, attached to an ionised aromatic ring, into a methyl group bound to an ionised cycloheptatriene ring.

In order to test this hypothesis, it is necessary to examine a system containing a methyl and an ethyl group attached to an aromatic nucleus. Ionised *p*-ethyltoluene is a suitable system; moreover, $^{\cdot}CH_3$ loss from the molecular ion of this compound has previously been investigated using ^{2}H-labelling.[21] These experiments reveal that both methyl groups are involved in $^{\cdot}CH_3$ loss; however, the methyl group originally incorporated in the ethyl side chain is eliminated predominantly (to roughly five times the extent of that originally attached to the aromatic nucleus). Furthermore, no loss of integrity of either methyl group occurs.[21] These data are consistent with rate-determining rearrangement of ionised *p*-ethyltoluene to ionised dimethylcycloheptatriene structures followed by relatively fast elimination of $^{\cdot}CH_3$. The preference for loss of the methyl group which was part of the original ethyl chain may be explained using the mechanism given in Scheme 3. After the rate-determining rearrangement, an ion of structure (9) is formed; the original β-methyl group becomes attached to the sp^3 carbon atom in the ionised dimethylcycloheptatriene (9). Direct cleavage of this radical cation, thus eliminating $^{\cdot}CH_3$, can occur only if the original β-methyl group is lost. A rearrangement [(9) ⟶ (10)] must occur prior to elimination of the α-methyl group. After the rate-determining isomerisation, (8) ⟶ (9), discrimination against this rearrangement will take place; direct cleavage of (9), resulting in loss of the β-methyl group, will be favoured because it may proceed faster. Hence, the preference for elimination of the β-methyl group in decomposition of ionised *p*-ethyltoluene may be explained.

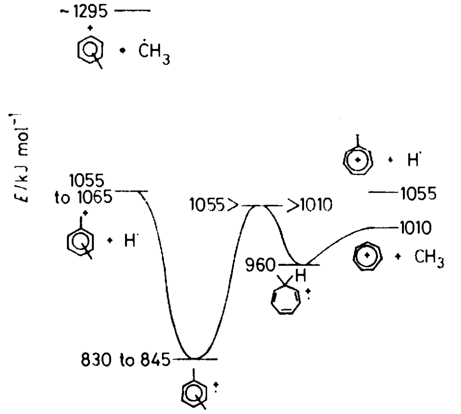
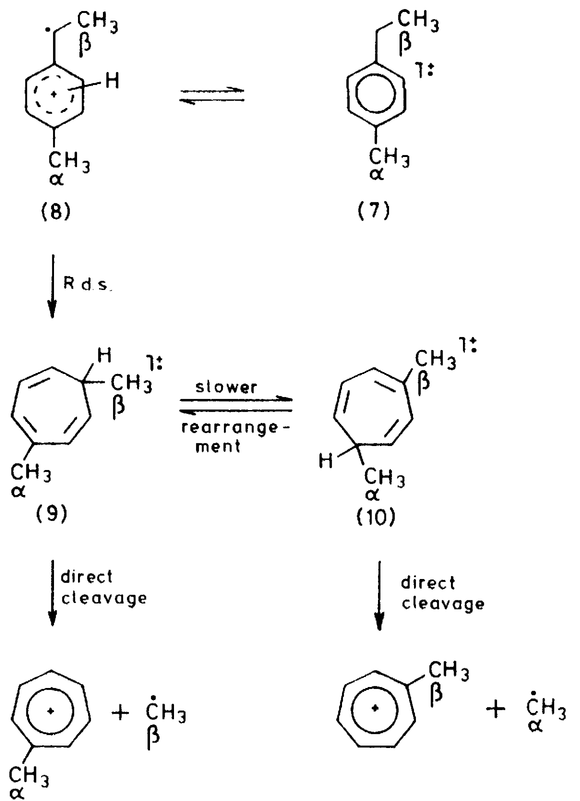


FIGURE 7 Potential energy profile for isomerisation and dissociation of ionised xylenes and methylcycloheptatriene



SCHEME 3

The activation energy for the proposed ring expansion of ionised *p*-ethyltoluene may be estimated by a similar procedure to that employed above for ionised ethylbenzene. The value obtained is *ca.* 170 kJ mol^{-1}. This figure is somewhat higher than that found for the lower homologue, ionised ethylbenzene, where a range of 85—135 kJ mol^{-1} was deduced for the activation energy for ring expansion. This increase probably reflects mainly the reduction in heat of formation of ionised *p*-ethyltoluene (805 kJ mol^{-1}) compared with ionised ethylbenzene (875 kJ mol^{-1}). A similar trend may be discerned for ionised toluene and xylenes. Again the activation energy for ring expansion (105—190 and 170—220 kJ mol^{-1}, respectively, for ionised toluene and xylenes) appears to increase upon further substitution of the aromatic ring. This may likewise be interpreted in terms of the rather large stabilisation conferred upon ionised toluene by substitution of a methyl group for a ring hydrogen atom (heats of formation of ionised toluene and ionised xylenes are 900 and 830—845 kJ mol^{-1}, respectively).

Nevertheless, despite this trend, it does indeed appear likely that ring expansion processes in a given ionised aromatic system have lower activation energies when ethyl, rather than methyl, groups are involved. In the case in question, ionised *p*-ethyltoluene, ring expansion involving the α-methyl group does not occur to a significant extent at energies appropriate to slow dissociations. This follows since both methyl groups retain their identities; ring expansion involving the α-methyl group would lead to loss of integrity of this unit and is therefore excluded.

Further experimental evidence may be cited in favour of this hypothesis; relevant data concerning the decomposition, *via* $^{\bullet}CH_3$ loss, of three isomers of $C_9H_{12}^{+\bullet}$ are given in Table 4.

TABLE 4

Average kinetic energy releases and measured transition state energies associated with methyl radical loss from some isomers of $C_9H_{12}^{+\bullet}$

Precursor	Average kinetic energy release [a] (kJ mol^{-1})	Measured transition state energy (kJ mol^{-1})
Isopropylbenzene	6.0	[b]
p-Ethyltoluene	9.0	1 005
Mesitylene	18.2	1 040

[a] Measured from second field-free region metastable peaks. [b] Data not available.

Although there are serious problems in determining accurate appearance potentials on standard mass spectrometers,[22,23] large differences are probably significant. The values obtained for the transition state energies for $^{\bullet}CH_3$ loss from ionised *p*-ethyltoluene and mesitylene differ by 35 kJ mol^{-1}, that for ionised mesitylene being the greater. Moreover, the average[5] kinetic energy releases associated with these reactions also differ appreciably; $^{\bullet}CH_3$ loss from ionised mesitylene releases roughly twice as much kinetic energy than does $^{\bullet}CH_3$ elimination from ionised *p*-ethyltoluene. This increase in the kinetic energy release accompanying $^{\bullet}CH_3$ loss may be discerned directly from the metastable peaks for the processes concerned, Figure 8. These data are consistent with $^{\bullet}CH_3$ loss from both isomers of $C_9H_{12}^{+\bullet}$ occurring through the same channels but with more excess internal energy starting from ionised mesitylene. The most plausible explanation is that both ionised mesitylene and *p*-ethyltoluene undergo rate-determining rearrangement to ionised dimethylcycloheptatriene isomers. However, the transition state energy involved in the isomerisation of ionised mesitylene is greater, thus giving rise to more average kinetic energy release than found for ionised *p*-ethyltoluene. This is also consistent with the measured transition state energies.

Using a similar procedure to that employed above for ionised xylenes and *p*-ethyltoluene, a value of *ca.* 200 kJ mol^{-1} may be deduced for the activation energy for ring expansion of mesitylene. This value is, as expected, higher than that found for ionised *p*-ethyltoluene.

It is interesting to note that the average kinetic energy release associated with $^{\bullet}CH_3$ loss from ionised isopropylbenzene is the smallest observed for any of the $C_9H_{12}^{+\bullet}$ isomers examined (Table 4). Two possible explanations may be advanced for this phenomenon; first, $^{\bullet}CH_3$ elimination occurs by direct cleavage of a benzylic bond. Alternatively, ring expansion may occur, *via* a lower energy transition state than that appropriate to *p*-ethyltoluene, to form ionised dimethylcycloheptatriene which may then eliminate $^{\bullet}CH_3$. It is not possible at this stage to differentiate between these two explanations. In the light of the above discussion, it may be concluded that loss of $^{\bullet}CH_3$ from ionised t-butylbenzene ought to occur *via* a lower energy transition state than $^{\bullet}CH_3$ elimination from ionised durene. The most sensitive test for this prediction is the kinetic energy release which is associated with the reactions; the average kinetic energy release should be smaller for $^{\bullet}CH_3$ loss from ionised t-butylbenzene. This prediction is confirmed by experiment; $^{\bullet}CH_3$ loss from ionised durene releases roughly five times more kinetic energy than $^{\bullet}CH_3$ elimination from ionised t-butylbenzene (average values 22 and 4 kJ mol^{-1}, respectively). The difference in kinetic energy release is clearly evident from

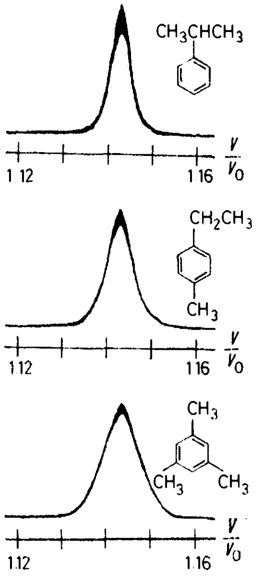


FIGURE 8 First field-free region metastable peaks for methyl radical loss from some isomers of $C_9H_{12}^{+\bullet}$; the abscissae have a similar significance to those of Figure 5

the metastable peaks for the processes concerned (Figure 9).

Conclusion.—It is found that halogen and methyl radical losses from halogeno- and alkyl-aromatic molecular ions frequently occur after ring expansion to ionised cycloheptatriene structures. In some cases, this ring expansion is rate-determining. The activation energy for the ring expansion varies according to the structure of the ion, typical values being in the range 100—200 kJ mol^{-1}. In the alkyl-aromatic series, the ease of ring expansion appears to increase as the degree of branching at the benzylic position increases.

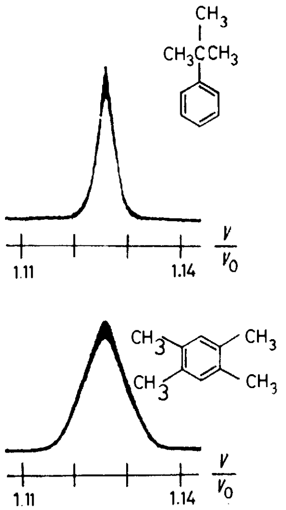


FIGURE 9 First field-free region metastable peaks for methyl radical loss from two isomers of $C_{10}H_{14}^{+\cdot}$; the abscissae have a similar significance to those of Figure 5

EXPERIMENTAL

All mass spectra were recorded using an AEI MS902 mass spectrometer; samples were introduced using the all glass heated inlet system (AGHIS) and run at a source pressure of *ca.* 10^{-6} Torr. The pressure in the analysers was *ca.* 10^{-7} Torr, or less, thus precluding significant collision-induced dissociations. The accelerating voltage was usually 8 kV and the nominal electron beam energy was 70 eV.

The kinetic energy release values were computed from the width at half-height of second field-free region metastable peaks; no correction was applied for the width of the main beam.

Dissociation of metastable ions in the first field-free region was observed by increasing the accelerating voltage at constant electric sector voltage and magnetic field strength.[24] The appearance potentials were measured on metastable ions dissociating in the first field-free region; the internal calibrant employed was the molecular ion of 2-chloropropane (appearance potential 10.8 eV[13]) and the results were evaluated using the semi-log plot method.[25] These metastable ions were observed by reducing the electric sector voltage at constant magnetic field strength and accelerating voltage [26] in order to increase sensitivity.

Financial support from the S.R.C., Shell Research, and Sidney Sussex College, Cambridge (Research Fellowship to R. D. B.) is gratefully acknowledged. The gift of a sample of 7-methylcyclohepta-1,3,5-triene from Drs. T. A. Molenaar-Langeveld and N. M. M. Nibbering is acknowledged with thanks.

[8/1662 *Received*, 19*th September*, 1978]

REFERENCES

[1] D. H. Williams, *Accounts Chem. Res.*, 1977, **10**, 280.

[2] H. M. Rosenstock, V. H. Dibeler, and F. N. Harllee, *J. Chem. Phys.*, 1964, **40**, 591.

[3] R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam, 1973.

[4] D. H. Williams and R. D. Bowen, *J. Amer. Chem. Soc.*, 1977, **99**, 3192.

[5] D. T. Terwilliger, J. H. Beynon, and R. G. Cooks, *Proc. Roy. Soc.*, 1974, **A341**, 135.

[6] G. Hvistendahl and D. H. Williams, *J. Amer. Chem. Soc.*, 1975, **97**, 3097.

[7] See, for example, 'Mass Spectrometry,' ed. R. A. W. Johnstone (Specialist Periodical Report), The Chemical Society, London,' vol. 4, 1977, pp. 38ff. and references cited therein.

[8] H. M. Grubb and S. Meyerson, 'Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York, 1963, p. 453.

[9] I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1971, **93**, 99.

[10] H. J. Beynon, J. E. Corn, W. E. Battinger, R. M. Caprioli, and R. A. Benkeser, *Org. Mass Spectrometry*, 1970, **3**, 1371.

[11] M. J. S. Dewar and D. Landman, *J. Amer. Chem. Soc.*, 1977, **99**, 2446.

[12] J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 1070; *J. Chem. Phys.*, 1953, **21**, 2029.

[13] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 'Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,' National Bureau of Standards, Washington, D.C., 1969.

[14] J. Winkler and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1973, **95**, 7533.

[15] F. W. McLafferty and J. Winkler, *J. Amer. Chem. Soc.*, 1974, **96**, 5182.

[16] R. C. Dunbar, *J. Amer. Chem. Soc.*, 1975, **97**, 1382.

[17] I. Howe, N. A. Uccella, and D. H. Williams, *J.C.S. Perkin II*, 1973, 249.

[18] A. Venema, N. M. M. Nibbering, and Th. J. de Boer, *Tetrahedron Letters*, 1971, 2141.

[19] J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, 1977, **99**, 5417.

[20] J. B. Farmer, F. P. Lossing, D. G. H. Marsden, and C. A. McDowell, *J. Chem. Phys.*, 1956, **24**, 52.

[21] F. Meyer and A. G. Harrison, *J. Amer. Chem. Soc.*, 1964, **86**, 4757.

[22] J. H. Beynon, R. G. Cooks, K. R. Jennings, and A. J. Ferrer-Correia, *Internat. J. Mass Spectrometry Ion Phys.*, 1975, **18**, 87.

[23] H. M. Rosenstock, *Internat. J. Mass Spectrometry Ion Phys.*, 1976, **20**, 139.

[24] K. R. Jennings, *J. Chem. Phys.*, 1965, **43**, 4176.

[25] F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, 1951, **19**, 1254.

[26] F. W. McLafferty, J. Okamoto, H. Tsuyama, Y. Nakajima, T. Noda, and F. W. Major, *Org. Mass Spectrometry*, 1969, **2**, 751.