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Rearrangements of Toluene and Cycloheptatriene Cations

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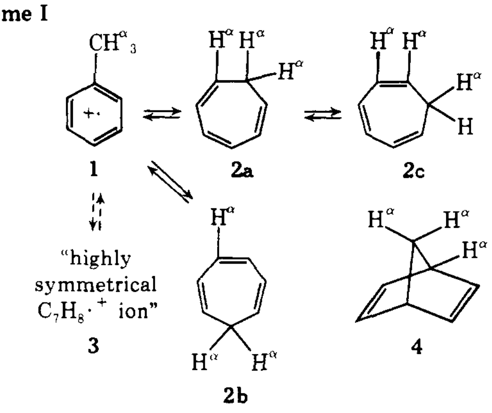
Abstract: The losses of CH_3 and CH_6 from the gaseous toluene cation (**1**) have been studied using seven isotopic isomers of **1** and two of cycloheptatriene (**2**) utilizing high resolution (1:50000) measurement of the abundance of the isobaric ionic products. Four distinct isomerization pathways, competitive with other **1** reactions, can be identified: (i) scrambling of the ring hydrogen atoms without involvement of the methyl group; (ii) isomerization **1** $\rightleftarrows$ **2** possibly through norcaradiene (**7**) as an intermediate; (iii) single exchange of an α-H and ring-H, possibly through methylenecyclohexadiene (**8**) as an intermediate; and (iv) complete scrambling of carbon as well as hydrogen atoms, possibly through opening of the aromatic ring. Reaction ii appears to involve the tightest activated complex, and i and ii the lowest activation energy; iii is intermediate, while iv has the loosest activated complex and highest activation energy. An additional pathway for the isomerization of **2**, possibly through bis(methylene)cyclopentene (**10b**), is also indicated.

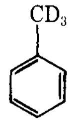
Most unimolecular decompositions of simple aromatic and related cations are accompanied by extensive rearrangement.[3-9] A number of detailed studies, some utilizing multiple isotopic labeling, have shown that decompositions of benzene,[5] toluene (**1**),[6,8,9] and cycloheptatriene (**2**)[7,8] molecular ions can involve the loss of virtually all positional identity of the carbon as well as the hydrogen atoms. However, the mechanisms of such rearrangements remain obscure;[4] most labeling studies have provided little information of the pathways involved because of the completeness of scrambling in the products. From their recent double-^{13}C-labeling study, Davidson and Skell conclude,[7] "This observation leaves in total obscurity the mechanism of carbon scrambling in toluene."

A common suggestion for the behavior of toluene and isomeric $C_7H_8\cdot^+$ cations is that their molecular rearrangements involve (Scheme I) isomerization to a common structure such as cycloheptatriene (**2a** or **2b**),[10] or a more symmetrical ion (**3**),[3] with hydrogen scrambling in **2a** involving H migration through **2c**.[5,10-12] The observation[7] that norbornadiene (**4**) undergoes ready loss of C_2H_2 with only minor carbon scrambling makes this a less probable intermediate for the isomerization of either **1** or **2**. Recent evidence[8] indicates that the interconversion **1** $\rightleftarrows$ **2** is rapid at the threshold energy for hydrogen loss, making mechanistic studies at these energies difficult. At higher energies, decomposition can take place before such isomerization is complete;[8,12] however, studies at higher energies utilizing hydrogen loss reactions are compromised because the resulting benzyl and tropylium ions of higher internal energies also undergo rapid interconversion.[8]

In this report we conclude that isotopic scrambling arises through at least four competitive pathways (Scheme II) whose relative rates are strongly energy dependent. These conclusions are based on the study of $C_7H_8\cdot^+$ decompositions involving the loss of only one carbon atom. Although these product ions are of relatively low abundance, formation of $C_6H_5^+$ and $C_6H_2\cdot^+$ require approximately 1 eV less and 5 eV more energy, respectively, than formation of $C_5H_5^+$, the reaction which has been used to demonstrate scrambling in most previous studies. Also an early report by Rylander and Meyerson[13] indicated that $C_6H_5^+$ formation from toluene involves only partial hydrogen scrambling. We wished to probe the scrambling pathways utilizing the isoto-

Scheme I

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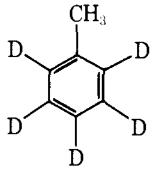
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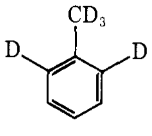
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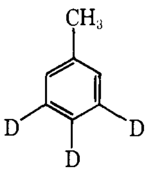
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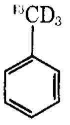
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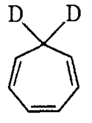
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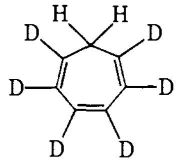

g

pic distribution of these product ions; of course such results will only be indicative of the isomerization reactions which are truly competitive with formation of these ions. Although the presence of isolated electronic states has been postulated in particular cases,[14-16] other evidence indicates that most unimolecular dissociations of toluene and similar aromatic cations occur from the ground electronic state and follow the predictions of the quasiequilibrium theory.[15-18] This point is critical to our conclusions, and additional evidence for the negligible importance of isolated states will be presented here.

In the original study,[13] the abundances of the *m/e* 76-79 ions in the mass spectra of toluene-*o-d*, *-m-d*, and *-p-d* were found to be virtually identical, indicating loss of positional identity of the ring hydrogen atoms. Labeling of the ring and α positions indicated that the $C_6H_5^+$ ions contain an average of four of the original five ring hydrogens, but that an appreciable fraction of the $C_6H_5^+$ ions formed contain all three α hydrogen atoms. Further interpretation was hampered by the overlap of isobaric ions at each nominal mass. Here we have studied deuterium and carbon-13 labeled $C_6H_2^+$, $C_6H_3^+$, $C_6H_4^+$, and $C_6H_5^+$ ions formed from the labeled precursors a-g. High resolution (50,000) conditions were used to separate the isobaric multiplets; for example, the peak at *m/e* 77 in the mass spectrum of e is made up of the ionic species $C_6H_5^+$, $C_6H_3D\cdot^+$, $C_6HD_2^+$, $C_5{}^{13}CH_4\cdot^+$, $C_5{}^{13}CH_2D^+$, and $C_5{}^{13}CD_2\cdot^+$, whose mass values cover a range of only 7.56 mmu (77.03913-77.03156).

Experimental Section

All of the data were determined on a Hitachi RMH-2 double focusing mass spectrometer; a resolving power of 50,000 (10% valley) was used for the high resolution data. The relative abundance of each component of a multiplet was determined by making two sets of ten scans over each peak. For each ion studied, the two average values were equal to within 95% confidence levels, and these were further averaged. The appearance potential data for toluene (Table I) were determined by the semilogarithmic plot technique,[19] using the literature values for $C_7H_8\cdot^+$ and $C_7H_7^+$ as standards.

All samples were purified by gas chromatography and introduced into the mass spectrometer at approximately 150°C. Toluene-α,α,α-d_3 (a), toluene-*2,3,4,5,6*-d_5 (b), and toluene-d_8 were commercial samples (Merck and Co., 99 atom % deuterium).

Toluene-α,α,α,*2,6*-d_5 (c). 2,6-Dichlorobenzoic acid (Aldrich) was reduced with lithium aluminum deuteride ($LiAlD_4$) in ether to 2,6-dichlorobenzyl-α,α-d_2 alcohol. After exchange of the alcohol hydrogen with deuterium by evaporation of CH_3OD from the sample several times, the alcohol was reduced with D_2 in the presence of 10% palladium on carbon and 95% of the required triethylamine to neutralize the HCl produced in CH_3OD solution. The purity of the product was checked by mass spectrometry at low ionizing voltage (LeV-MS); d_3, 12%; d_4, 14.5%; d_5, 83.7%; d_6, 0.5%. Proton NMR indicated <2% hydrogen in the methyl group.

Toluene-*3,4,5*-d_3 (d). The diazonium salt of 4-aminotoluene-

Scheme II

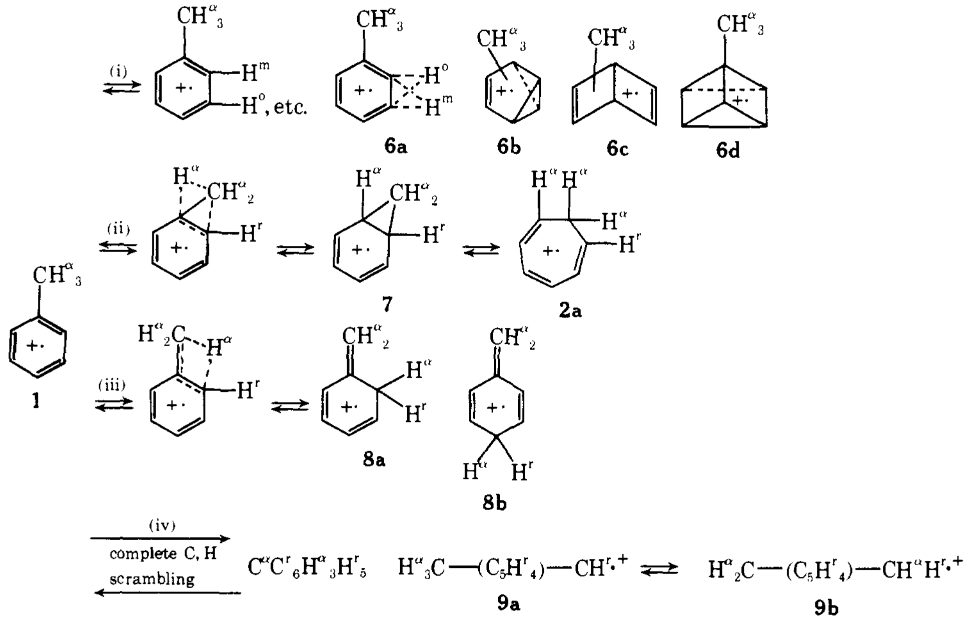


Table I. Appearance Potentials and Partial 70-eV Mass Spectra of Toluene and Toluene-d_8

Toluene			Toluene-d_8		Isotope effect, $[C_xH_y^+]/[C_7H_8\cdot^+]$
Ion	AP, eV	% Σ ions	Ion	% Σ ions	$[C_xD_y^+]/[C_7D_8\cdot^+]$
C_7H_8	8.8[a]	21.8	C_7D_8	27.0	1.00
C_7H_7	11.8[a]	41.5	C_7D_7	41.1	1.25
C_6H_5	14.9[b]	0.434	C_6D_5	0.481	1.12
C_6H_4	16.2	0.161	C_6D_4	0.147	1.36
C_6H_3	18.8	0.265	C_6D_3	0.234	1.40
C_6H_2	21.0	0.404	C_6D_2	0.371	1.35

[a] Reference 20, which also reports an appearance potential of 15.7 eV for $C_5H_5^+$. [b] Literature value 13.7 eV.[a]

Table II. $C_6(H,D)_5^+$ Species from Deuterated Toluenes

Compd and mechanism	Abundances (%) of isotopic peaks			
Statistical[b]	1.8	26.8	53.6	17.9
	$C_6H_5^+$	$C_6H_4D^+$	$C_6H_3D_2^+$	$C_6H_2D_3^+$
Toluene-α,α,α-d_3 (a)	42.8 ± 1.0[a]	25.0 ± 1.4	23.0 ± 1.3	9.2 ± 0.7
Calcd[d]	41.5	24.7	25.2	8.6
Toluene-α,α,α-d_3, 15 eV	17	39	32	12
Toluene-*3,4,5*-d_3 (d)	0.8[c]	12.8 ± 1.4	32.4 ± 2.6	54.0 ± 2.1
Calcd, ring unscrambled[d]	0.8	12.4	26.6	60.2
Calcd, ring scrambled[d]	0.8	12.7	33.4	53.4
	$C_6D_5^+$	$C_6HD_4^+$	$C_6H_2D_3^+$	$C_6H_3D_2^+$
Toluene-*2,3,4,5,6*-d_5 (b)	39.7 ± 1.0	25.5 ± 1.1	25.4 ± 1.1	9.4 ± 0.4
Calcd[d]	40.8	25.1	26.1	8.0
Toluene-α,α,α,*2,6*-d_5 (c)	0.9[c]	13.7 ± 0.7	32.7 ± 1.3	52.7 ± 1.2
Calcd, ring unscrambled[d]	1.0	12.5	24.3	62.2
Calcd, ring scrambled[d]	0.9	12.9	32.1	54.1

[a] 95% confidence limits for 20 determinations. [b] Calculated values assuming statistical H/D scrambling and no isotope effects. [c] Estimate; intensity was too low for accurate measurement. [d] Calculated values assuming k(complete H/D scrambling)/k(single H^r/H^α exchange) = 2.32 (2.36, ring unscrambled), and isotope effects for $CH_3C_6D_5/CD_3C_6H_5$, i(complete H/D scrambling) = 1.14, i(single H^r/H^α exchange) = 1.00.

3,5,N,N-d_4 was prepared in D_2O[21] and reduced to the desired product with $SnCl_2$ in D_2O.[22] LeV-MS gave d_2, 15%; d_3, 80%; d_4, 5%.

Toluene-α-^{13}C-α,α,α-d_3 (e). Reduction of benzoic acid-^{13}C (Isomet Corp., 66% ^{13}C in carbonyl carbon) with $LiAlD_4$ and then with D_2 as for c but without the presence of triethylamine gave the desired product. LeV-MS gave 64% excess ^{13}C. Proton NMR showed <2% hydrogen in the methyl group.

Cycloheptatriene-*2,3,4,5,6,7*-d_6 (g). Diazomethane was generated from nitrosomethylurea[23] with benzene-d_6 as solvent, dried over KOH, and added dropwise to a mixture of benzene-d_6 and Cu_2Br_2 with stirring and gentle refluxing.[24] Distillation in the presence of hydroquinone gave the product: d_4, 4%; d_5, 5%; d_6, 91% (LeV-MS); proton NMR in $CDCl_3$ solution gave a single broad line at δ 2.25.

Cycloheptatriene-*1,1*-d_2 (f). A solution of dideuteriodiazomethane in ether was prepared from diazald (Aldrich), carbitol-d, NaOD, and D_2O.[24] This was added to Cu_2Cl_2-benzene as described above. After an initial fractionation, the product was separated by gas chromatography: d_0, 3%; d_1, 14%; d_2, 83% (LeV-MS).

Results and Discussion

Isotope Effect on Methyl Loss. To determine the magnitude of any deuterium isotope effect on methyl loss from toluene without the complication of H/D scrambling, the mass spectra of toluene and toluene-d_8 were compared (Table I). The isotope effect is relatively small (<1.5) in all cases, indicating that hydrogen loss is not involved in the rate-determining step. The value of 1.12 observed for the formation of $C_6H_5^+$ is consistent with the secondary isotope effect which would result from the loss of methyl in the rate-determining step; we will assume that this is due to an isotope effect of 1.04 for each of the α-deuterium atoms.

Methyl Loss from Toluene. Consistent with Meyerson's findings,[13] the relative intensities of the $C_6(H,D)_5^+$ species for a, b, c, and d (Table II) differ substantially from the statistically predicted ratios calculated for complete hydrogen-deuterium scrambling prior to methyl loss. If scrambling were complete, the $C_6(H,D)_5^+$ abundances from $C_6H_5CD_3$ and $C_6H_2D_3CH_3$ and from $C_6D_5CH_3$ and $C_6H_3D_2CD_3$, should be identical. At energies near threshold, scrambling is increased, but is still incomplete. This is consistent with the conclusion[8] that the high degree of scrambling observed in $C_7H_7^+$ ions formed by the decomposition of higher energy $M\cdot^+$ ions from toluene is due in substantial part to the subsequent isomerization of the $C_7H_7^+$ ions.

For methyl loss from $C_6H_5CD_3$, the $C_6H_2D_3^+$ ions should arise from molecular ions which have undergone complete H/D scrambling (path iv, Scheme II). This is borne out by the data for the $C_6H_3D_2^+$ ions; their intensity relative to that of $C_6H_2D_3^+$ (2.6) is nearly that expected from the statistically calculated ratio (3.0). However, this is not the case for the $C_6H_4D^+$ ions; approximately half of these must arise from another process involving interchange of one ring hydrogen and one α-deuterium ("single H^r/H^α exchange," such as path ii or iii, Scheme II). The rate of this reaction relative to path iv approximately doubles at low electron energy, consistent with a lower activation energy and tighter activated complex for the former reaction. Most of the $C_6H_5^+$ ions from a should result from direct cleavage of C_6H_5-$CD_3\cdot^+$ before any H/D exchange takes place. The data for the complementarily labeled $C_6D_5CH_3$ (b) support these general conclusions. After correction for the secondary isotope effect, the two ions expected from complete scrambling, $C_6H_2D_3^+$ and $C_6H_3D_2^+$, are in the same ratio (2.6) as their counterpart products from $C_6H_5CD_3$, showing that there is no appreciable isotope effect on the rates for the formation of these ions relative to

Table III. $C_6(H,D)_5^+$ and $^{13}CC_5(H,D)_5^+$ from Toluene-α-^{13}C-α,α,α-d_3 (e)

Product	Calcd Model i	ii	iii	iv	Measured
$C_6H_5^+$	42.8	6.1	42.1	42.1	43.9 ± 2.8[a]
$C_6H_4D^+$	25.0	3.6	3.6	13.9	16.5 ± 2.1
$C_6H_3D_2^+$	23.0	3.3	3.3	3.3	3.1 ± 2.1
$C_6H_2D_3^+$	9.2	1.3	1.3	1.3	0.0 ± 0.7
$^{13}CC_5H_5^+$	0	36.7	0.7	0.7	1.9 ± 1.4[b]
$^{13}CC_5H_4D^+$	0	21.4	21.4	11.1	9.3 ± 1.2[b]
$^{13}CC_5H_3D_2^+$	0	19.7	19.7	19.7	17.2 ± 1.4[b]
$^{13}CC_5H_2D_3^+$	0	7.9	7.9	7.9	8.0 ± 1.2[b]

[a] Standard deviation, eight determinations. [b] Corrected for naturally occurring carbon-13.

each other. However, there is an isotope effect on their formation in competition with methyl loss from the toluene ion before isomerization. The complete scrambling reaction is favored in the precursor with hydrogen atoms on the methyl group, consistent with C-H bond rupture as a rate-determining step in path iv.

Isotopic data on the methyl loss species from toluene-α-^{13}C-α,α,α-d_3 (e) were also measured (Table III) to study the carbon scrambling accompanying these decompositions. The data for toluene-α,α,α-d_3 (Table II) were used to calculate the values expected with four possible models for carbon scrambling:

(i) No carbon scrambling.

(ii) Complete carbon scrambling.

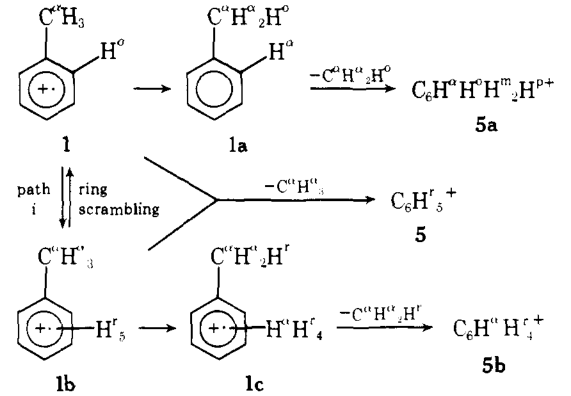
(iii) No carbon scrambling in the species showing no H/D scrambling, but complete carbon scrambling in the species showing single H^r/H^α exchange and those resulting from complete H/D scrambling.

(iv) No carbon scrambling in the species showing no H/D scrambling and single H^r/H^α exchange, but complete carbon scrambling in the species showing complete H/D scrambling.

Comparison of the calculated and measured values gives strong support to the last hypothesis; the small discrepancies can be rationalized by assuming that the carbon scrambling is not entirely complete for the species which have undergone complete H/D scrambling. Thus the complete H/D scrambling cannot result from just the repetition of the single H^r/H^α exchange reaction for a mechanism such as **1** ⇄ **7** (path ii) or **1** ⇄ **8a** (path iii); further, the single H^r/H^α exchange cannot involve an intermediate such as **3** which does not contain the $C^\alpha H^\alpha{}_2$ group.

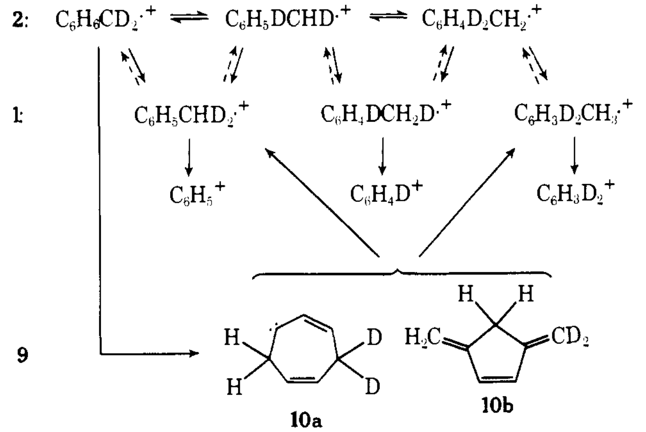
The single H^r/H^α exchange reaction, occurring without C^r/C^α exchange, makes possible the study of competitive processes (such as path i, Scheme II) involving scrambling of the ring hydrogen atoms; the reactions used in previous labeling studies of toluene[3,4,6] involve complete carbon as well as hydrogen scrambling. For compounds c and d, the α and ortho hydrogens have been isotopically distinguished from the other ring hydrogen atoms; the methyl loss data for c and d were compared with those for a and b, respectively (Table II). If the ring hydrogen atoms do not isomerize, a single exchange of the ortho and α hydrogens of c and d would not affect the isotopic identity of the product **5a** (Scheme III). Thus the product distribution should be different for the cases in which the rate of ring hydrogen scrambling (path i), as compared with the rate of single H^r/H^α exchange, is either (A) slow, so that **1** → **1a** → **5a** is the dominant pathway, or (B) fast, so that **1** → **1b** → **1c** → **5b** is the dominant pathway. Calculations of distributions expected for these cases were based on the following reasoning. Using k_H/k_D = 1.04 for the methyl loss reaction, **1** → **5**, and assuming a negligible deuterium isotope effect for **1** → **1a** or **1b** → **1c** when the reaction involves the exchange of H and D (vide infra), the data for a and b (Table II) are consistent with k_H/k_D = 1.14 for the complete scrambling reaction and with k(complete scrambling)/k(single H^r/H^α exchange) = 2.36 for case A (2.32 for case B at 70 eV, 1.2 at 15 eV). Application of these values gives the $C_6(H,D)_5^+$ product distributions for c and d shown in Table II, strongly supporting case B.[25] Thus the processes which can cause scrambling of the ring hydrogen atoms include one that does not involve the methyl group (path i, Scheme II), in contrast to those proposed previously for toluene (**1** ⇄ **2**, **1** ⇄ **3**, Scheme I). The mechanism of path i could involve ring H exchange of adjacent carbon atoms (**6a**), or could be similar to that suggested for benzene[5] involving equilibration through valence isomers such as **6b** → **6d**.

Scheme III



For the single H^r/H^α exchange reaction, **1b** → **1c**, the calculated results for a–d (Table II) are independent of which of the possible reaction intermediates, such as **2a**, **4**, **7**, or **8**, are postulated on the assumption that any such intermediate which involves a substantially bent C-H-C bond in the transition state would lead to a negligible isotope effect.[26] Based on previous work,[3-12] the two most attractive intermediates for the single H^r/H^α exchange would appear to be the norcaradiene ion (**7**) and the methylenecyclohexadiene ion (**8a**)[8,27] (paths ii and iii, Scheme II). The former is analogous to the intermediate found[28] in the thermal conversion of cycloheptatriene molecules to toluene. For **1** and **2** ions of internal energies much lower than those which lose methyl, the interconversion **1** ⇄ **2** occurs readily[8,9] so that a reaction pathway such as ii must be important; formation of the corresponding intermediate (which presumably is **7**) from **1** should require a relatively low activation energy. If this is due to the concerted formation and cleavage of several bonds as shown in Scheme II, this reaction should also have a relatively tight activated complex. A study of the methylenecyclohexadiene ion (**8a**) shows[27] that it has a substantially lower tendency for hydrogen scrambling than either of the isomeric **1** or **2** ions; thus pathway iii should have a higher activation energy than ii. From Scheme II, it would appear logical that the activated complex for **1** ⇄ **8a** should be looser than that for **1** ⇄ **7**. (The isomeric methylenecyclohexadiene (**8b**) is also a possible intermediate; its energetic requirements should be similar to those of **8a**, but it could have a less favorable activated complex configuration.) However, one aspect of path ii makes it a questionable choice as the principal mechanism for single H^r/H^α exchange for the higher energy **1** ions undergoing CH_3 loss; the proposed[10] cycloheptatriene isomerization **2a** → **2c** would cause scrambling of carbon as well as hydrogen atoms, which is not observed for this reaction. To clarify this, the analogous reactions of labeled cycloheptatrienes

Scheme IV



were also investigated.

Methyl Loss from Cycloheptatriene. The commonly postulated pathway ii for hydrogen scrambling in toluene, **1** ⇄ **2**,[6,8,10] was tested utilizing the labeled cycloheptatrienes f and g; the methyl loss data are given in Table IV. The amount of unscrambled product is much lower than that for **1** (Table II), indicating that a substantial amount of scrambling takes place *before* isomerization to toluene (assuming that most methyl loss occurs from **1**).[29] Thus conversion to **2a** cannot provide a significant pathway for the single H^r/H^α exchange reaction, **1b** → **1c**, and the pathway **1** ⇄ **7** must also be improbable for this, as the reaction **7** → **2** should have a relatively loose activated complex. Pathway iii thus appears to provide the most plausible mechanism for the single H^r/H^α exchange reaction; this is supported by recent evidence[8] that substituted toluene molecular ions of higher internal energy isomerize to substituted methylenecyclohexadiene ions.

Calculations were made of the $C_6(H,D)_5^+$ abundances expected from f and g if there were complete H/D scrambling in **2** (such as **2a** ⇄ **2b**, **2c**[10-12,28]), followed by isomerization to **1** and methyl loss (Scheme IV). There should be no isotope effect on the interconversion of the **2** isotopic isomers, following the reasoning given for the isotopic scrambling of **1**. For the reaction **2** → **1**, $k_H/k_D = 1.6$ should be a logical value;[12a,27] calculations using $k_H/k_D = 2.0$ show that this choice has only a minor effect on the results (Table IV).[30] The experimental results are striking in two ways; there is a large isotope effect (compare $[C_6H_3D_2^+]$ from f with $[C_6H_2D_3^+]$ from g). Also, $C_6H_6CD_2\cdot^+$ (f) produces a *greater* abundance of $C_6H_3D_2^+$, supposedly the product of complete scrambling, than that predicted, despite the fact that the $C_6H_5^+$ abundance indicates that some of f decomposes without scrambling. This could be due to initial isomerization to intermediates such as **10a** or **10b**, which could lose $CH_3\cdot$ at least as readily as $CHD_2\cdot$. Thus the behavior of **2** is in direct contrast to that of the **1** ions, making cycloheptatriene an illogical intermediate for any substantial proportion of the H/D scrambling processes of the toluene ion before methyl loss. Path ii must be of importance only for lower energy **1** ions, consistent with our previous conclusions.[27]

Table IV. $C_6(H,D)_5^+$ Species from Deuterated Cycloheptatrienes

Compd	Abundances (%) of isotopic peaks		
	$C_6H_5^+$	$C_6H_4D^+$	$C_6H_3D_2^+$
CHT-*1,1-d*$_2$ (f)	20.2 ± 1.2[a]	44.3 ± 2.5	35.5 ± 1.8
Calculated,[b] $k_H/k_D = 1.6$	13.7	55.0	31.3
$k_H/k_D = 2.0$	13.1	54.7	32.0
	$C_6D_5^+$	$C_6HD_4^+$	$C_6H_2D_3^+$
CHT-*2,3,4,5,6,7-d*$_6$ (g)	18.8 ± 1.3	55.7 ± 2.4	25.5 ± 1.2
Calculated,[b] $k_H/k_D = 1.6$	15.8	55.5	28.7
$k_H/k_D = 2.0$	17.1	54.9	27.6

[a] 95% confidence limits for 20 determinations. [b] Assuming complete scrambling of **2** (f or g) prior to isomerization to **1**; ratios of 15:55:30 would be expected if there were no isotope effect.

Table V. $C_6(H,D)_2\cdot^+$ Species from Deuterated Toluenes

Toluene-α,α,α-*d*$_3$ (a)	Toluene-*2,3,4,5,6-d*$_5$ (b)	Statistical
$C_6H_2\cdot^+$ 81.8[a] ± 2.1[b]	$C_6D_2\cdot^+$ 78.7 ± 2.2	10
$C_6HD\cdot^+$ 14.9 ± 0.9	$C_6HD\cdot^+$ 18.9 ± 0.6	15
$C_6D_2\cdot^+$ 3.3 ± 0.4	$C_6H_2\cdot^+$ 2.4 ± 0.4	3

[a] Adjusted for the H/D isotope effect on methyl loss (Table I) by increasing $[C_6D_2^+]$ values by 35% and $[C_6HD^+]$ values by 18%. [b] 95% confidence limits for 20 determinations.

Table VI. $C_6(H,D)_2\cdot^+$ Species from Toluene-α-^{13}C-α,α,α-*d*$_3$ (e)

Ion	Measured	Calcd[b]
$C_6H_2\cdot^+$	75.9 ± 4.9	73.5
$C_6HD\cdot^+$	4.5 ± 1.4	4.6
$C_6D_2\cdot^+$	0.9 ± 0.9	0.5
$^{13}CC_5H_2\cdot^+$	5.8 ± 1.4	7.3[a]
$^{13}CC_5HD\cdot^+$	9.8 ± 1.4	10.9[a]
$^{13}CC_5D_2\cdot^+$	3.1 ± 0.9	3.2[a]

[a] Corrected for naturally occurring ^{13}C. [b] Calculated using model iv, Table III.

$C_6H_2^+$ Formation from Toluene. The processes giving rise to the $C_6H_2^+$ ions in the mass spectrum of toluene should provide an interesting comparison, as these originate from molecular ions formed with approximately 6 eV more internal energy than those leading to the $C_6H_5^+$ ions (Table I). Several combinations of reaction sequences can yield $C_6H_2^+$ from $C_7H_8^+$; we have observed weak unimolecular metastable transitions corresponding to $C_6H_2^+$ formation from $C_6H_3^+$, $C_7H_7^+$, and $C_7H_8^+$. For compounds a and b, the measured peak intensities, adjusted to compensate for the isotope effect on $C_6H_2^+$ formation (Table I), are listed in Table V. The degree of scrambling has been greatly reduced in these higher energy ions, as expected from previous studies.[8,12a,27] The reduction in the complete H/D scrambling is proportionately less than that in the single H^r/H^α exchange, the latter being nearly eliminated.[31]

The formation of $C_6H_2\cdot^+$ from the doubly-labeled toluene e was also investigated (Table VI). Comparison of the results with those calculated using the model found to be applicable to methyl loss (iv) indicates again that carbon scrambling is associated with complete H/D scrambling.

Data for the less abundant ions $C_6(H,D)_3^+$ and $C_6(H,D)_4\cdot^+$, although of lower reliability, indicated a degree of scrambling intermediate between that for $C_6(H,D)_2^+$ and for $C_6(H,D)_5^+$, consistent with the appearance potentials of these ions (Table I).

Thus it appears that similar processes are involved in the toluene isomerization reactions preceding decomposition to form $C_6H_2\cdot^+$ and $C_6H_5^+$ and, possibly, $C_6H_3^+$ and $C_6H_4\cdot^+$, and that only the relative rates, not the nature, of these isomerization and decomposition reactions change despite the very wide range of internal energies of their precursor ions. It is thus unlikely that any of these ion species are formed from toluene ions in an isolated excited electronic state. Formation of $C_6H_5^+$ from **1** must also be in direct competition with formation of $C_7H_7^+$, which is responsible for the base peak in the mass spectrum of **1**. Toluene ions giving $C_7H_7^+$ (average ionizing electron energy 14 eV) have undergone 90% hydrogen scrambling before hydrogen loss, while toluene ions giving $C_7H_7^+$ which undergo metastable decomposition to produce $C_5H_5^+$ (A = 15.7 eV) have undergone 78% scrambling before H· loss.[27] The toluene ions of slightly lower energy (15 eV ionizing electrons, Table II) undergoing methyl loss exhibit a degree of scrambling intermediate between these values, while **1** ions of higher energy (70 eV ionizing electrons) losing methyl are only 60% scrambled. Thus the isomerization processes which the present data show to be competitive with $C_6H_2\cdot^+$ and $C_6H_5^+$ formation should be competitive with all but the lowest energy isomerization and decomposition processes of the toluene ion.[14-18]

Isomerization Pathways of Toluene Cations. We conclude that toluene ions can isomerize by a variety of mechanisms (Scheme II).

(i) **Ring Hydrogen Scrambling.** This process takes place more readily before methyl loss than does single H^r/H^α exchange so that this pathway must have a very low activation energy comparable or even lower than that of the path ii. As discussed above, ring hydrogen exchange (**6a**) or valence isomerization (**6b, 6c,** or **6d**) are possible mechanisms for ii.

(ii) **Cycloheptatriene Ion Formation, Possibly through the Intermediacy of the Norcaradiene Ion, $1 \rightleftarrows 7 \rightleftarrows 2$.**[10-12,28] Although this process is rapid at the appearance potential for $C_7H_7^+$, $A(C_7H_7^+)$ = 11.8 eV,[8] it is not important for ions undergoing methyl loss, $A(C_6H_5^+)$ = 14.9 eV, consistent with a tight activated complex as well as a low activation energy for this reaction. The results for f and g, Table IV, indicate that cycloheptatriene ions can also isomerize by several pathways (Scheme IV).

(iii) **Single H^r/H^α Exchange.** The cycloheptatriene cation (**2**) is not formed in this process. A possible mechanism involves isomerization to the methylenecyclohexadiene ion (**8a**) (Scheme III), which should be a looser complex, higher activation energy reaction than $1 \rightleftarrows 7$.

(iv) **Complete Scrambling of Carbon and Hydrogen.** This process occurs by a different mechanism requiring a higher activation energy and looser activated complex than single H^r/H^α exchange, such as would be involved in the opening of the aromatic ring, $1 \rightleftarrows$ **9a**. A variety of $C_7H_8\cdot^+$ isomers (**9a, 9b**) could be involved in such drastic scrambling; those other than **1** which lose $CH_3\cdot$ must contain a large number of rings and/or unsaturated bonds.

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References and Notes

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(29) For the hydrogen loss reaction to form $C_7H_7^+$, the amount of scrambling is also greater in **2** than in **1**.[12a]

(30) This calculation also assumes that the distribution of internal energies, P(E), of **1** ions undergoing $CH_3\cdot$ loss after isomerization from **2** is the same as P(E) for such ions when originally formed by electron ionization of **1**; the P(E) functions of the molecular ions formed by ionization of **1** and **2** are similar.[12a]

(31) Calculations performed as described above for the data of Table II give k(complete H/D scrambling)/k(single H^r/H^α exchange) ~ 10 compared with a value of 2.3 for the $C_6H_5^+$ ions formed using 70 eV electrons, 1.2 for 15 eV.