

Organic and Biological Chemistry

Unimolecular Decomposition of Toluene and Cycloheptatriene Molecular Ions. Variation of the Degree of Scrambling and Isotope Effect with Internal Energy^{1a}

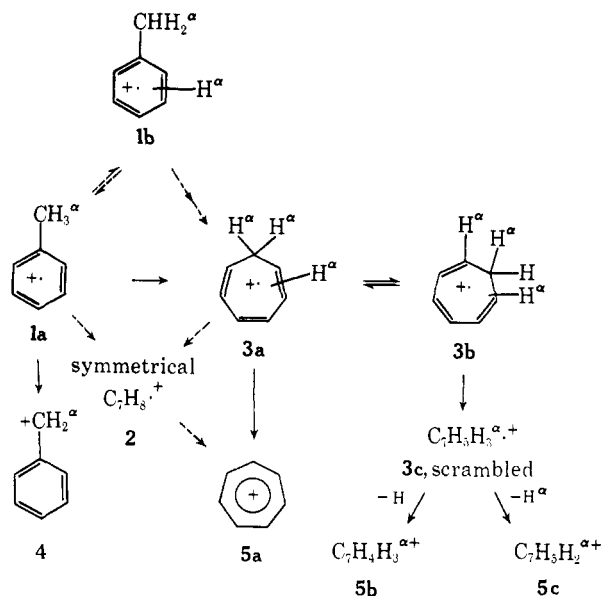
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Abstract: Quantitative measurements of the relative losses of H and D from the molecular ions of deuterated toluenes and cycloheptatrienes have been carried out for several definable ranges of precursor ion energies. The molecular ions appear to be completely scrambled in formation of the low-energy ions arising from unimolecular metastable transitions, but the degree of scrambling decreases with increasing internal energy and hence with decreasing lifetime. The deuterium isotope effect decreases with increasing internal energy; the observed values agree well with the theoretical values calculated by Vestal. The large isotope effect observed here for low-energy ions, particularly metastables, sounds a warning about the significance of deuterium-labeling studies where primary isotope effects are involved. The close similarity in the results for toluene and cycloheptatriene is consistent with Harrison's postulation of an initial isomerization of the toluene molecular ion to that of cycloheptatriene. The greatest differences are observed at high energies, indicating that here appreciable direct decomposition may be occurring from the unscrambled toluene molecular ion.

Although the importance of the internal energy of the precursor ion in determining the rate constant²⁻⁵ and the isotope effect⁶⁻⁸ in unimolecular ion decompositions is well known, utilization of these variables in mechanistic studies has been limited because of the experimental difficulties involved. In a preliminary communication⁹ we described techniques in which several different ranges of internal energies of the ions undergoing decomposition could be defined. This paper describes the application of these techniques to a study of the mass spectra of toluene and cycloheptatriene.

The formation of the abundant $C_7H_7^+$ ion from the toluene molecular ion, 1, has attracted a great deal of research interest since the classic work of Meyerson and coworkers indicated that this ion has the tropylium ion structure, 5, and that the hydrogen atoms of 1 lose their positional identity prior to the $C_7H_7^+$ formation.¹⁰ Thirteen other C_7H_8 isomers give mass spectra which



(1) (a) Metastable Ion Characteristics. XVII. Part XVI: D. J. McAdoo, F. W. McLafferty, and J. S. Smith, *J. Amer. Chem. Soc.*, **92**, 6343 (1970); (b) to whom correspondence should be addressed.

(2) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952); H. M. Rosenstock, *Advan. Mass. Spectrom.*, **4**, 523 (1968).

(3) A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 3582 (1969).

(4) F. W. McLafferty and R. B. Fairweather, *ibid.*, **90**, 5915 (1968).

(5) M. Vestal and G. Lerner, "Fundamental Studies Relating to the Radiation Chemistry of Small Organic Molecules," Aerospace Research Laboratory Report 67-0114, U. S. Defense Documentation Center, Alexandria, Va., 1967.

(6) M. Vestal and J. H. Futrell, *J. Chem. Phys.*, **52**, 978 (1970).

(7) C. Lifshitz and R. Sternberg, *J. Mass Spectrom. Ion Phys.*, **2**, 303 (1969).

(8) B. J.-S. Wang and E. R. Thornton, *J. Amer. Chem. Soc.*, **90**, 1216 (1968).

(9) I. Howe and F. W. McLafferty, *ibid.*, **92**, 3797 (1970).

(10) P. N. Rylander, S. Meyerson, and H. M. Grubb, *ibid.*, **79**, 842 (1957); H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.

are remarkably similar to that of toluene; the three of these isomers which have been studied by deuterium labeling, including cycloheptatriene, 3, also lose H positional identity in forming $C_7H_7^+$.¹¹ This and other evidence led Meyerson to conclude that all of these isomers first rearrange to a common $C_7H_8^+$ structure, 2, which resembles the cycloheptatriene isomer but is of even higher symmetry.¹¹ To explain the spectra of labeled methyl- and dimethylethylbenzenes Meyer and Harrison¹² have postulated instead an initial irreversible isomerization of the molecular ion to the cyclohep-

(11) S. Meyerson, *J. Amer. Chem. Soc.*, **85**, 3340 (1963); *Rec. Chem. Progr.*, **26**, 257 (1965).

(12) F. Meyer and A. G. Harrison, *J. Amer. Chem. Soc.*, **86**, 4757 (1964).

tatriene isomer,¹³ $1 \rightarrow 3$, in which a rapid hydrogen transfer can occur between the methylene and the adjacent carbon atoms, $3a \rightarrow 3b$.¹⁷ For the initial isomerization $1 \rightarrow 3a$ their data suggest that an α -H is transferred to the adjacent ring carbon atom, followed by insertion of the methylene group at random between any two ring carbon atoms. Scrambling of carbon as well as hydrogen atoms is complete for those ions with sufficient energy to undergo secondary decomposition to form $C_5H_5^+$, as shown from a study of toluene- α , I - $^{13}C_2$ by Rinehart and his coworkers.¹⁸

If $3a$ undergoes the hydrogen shift reaction, $3a \rightarrow 3b$, at a much faster rate than that for the hydrogen loss, $3a \rightarrow 5a$, the hydrogens will lose their positional identity. Scrambling of the hydrogens is not complete, however; this can be due to a competitive loss of α -H before or after isomerization of the toluene molecular ion ($1 \rightarrow 4$ ¹⁹ or $3a \rightarrow 5a$, respectively). For the latter possibility the data require that the rate of reaction $3a \rightarrow 3b$ is 20 times the rate of reaction $3a \rightarrow 5a$.¹²

Thus the mechanism for the formation of $C_7H_7^+$ must account for both the isomerization of the carbon skeleton and the scrambling of the hydrogen atoms. These can be accomplished essentially simultaneously by the formation of **2**, or separately by isomerization to $3a$ followed by scrambling through $3a \rightarrow 3b$. It is also possible to envisage a degree of H scrambling in **1**, $1a \rightarrow 1b$, before skeletal isomerization. To investigate these alternatives, we have compared the behavior of labeled toluenes and cycloheptatrienes of different internal energies. For example, more complete H scrambling in the products from **1** than **3** could be due to a contribution from reaction $1a \rightarrow 1b$, while less complete H scrambling could be explained by a contribution from reaction $1 \rightarrow 4$. Comparison of the behavior of **1** and **3** ions at different internal energies should increase the chance of detecting differences caused by separate decomposition pathways.

In view of the wide use of deuterated organic compounds in mass spectrometry to investigate site-specific transfers of hydrogen and/or scrambling mechanisms, it would be of great utility to determine the magnitude of primary deuterium isotope effects that might be anticipated. Substantial variations in these magnitudes

(13) In support of this postulate, it has been shown by molecular orbital calculations that there is little difference in the aromaticity of the radical cations **1** and **3**.¹⁴ The heats of formation of **4** and **5** are 216 and 209 kcal/mol, respectively, which would support the favorable decomposition of $C_7H_8^{+\cdot}$ from the cycloheptatriene rather than the toluene structure at energies close to threshold. However, heat of formation data derived from $C_7H_7^+$ appearance potentials indicate that this ion is formed with about 0.6 eV excess energy (toluene) and 1.0 eV excess energy (cycloheptatriene). Although an appreciable part of this excess energy may be due to the kinetic shift, the remaining energy is taken up by the reverse activation energy. Since this activation energy is not known for the recombination reactions, it is impossible to ascertain on this thermochemical evidence whether or not the lowest activation energy process for loss of hydrogen from the toluene molecular ion occurs via rearrangement to a cycloheptatriene structure.^{15,16}

(14) R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5780 (1968).

(15) J. L. Franklin, J. G. Dillard, H. M. Rosenbock, J. T. Herron, K. Drake, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969.

(16) A. G. Harrison in "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed., Interscience, New York, N. Y., 1970.

(17) See also S. Meyerson and E. K. Fields, *Org. Mass Spectrom.*, **2**, 1309 (1969), for comments on hydrogen scrambling in poly(methylbenzenes).

(18) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrell, *J. Amer. Chem. Soc.*, **90**, 2983 (1968).

(19) J. G. Burr and R. A. Meyer, *J. Chem. Phys.*, **40**, 2046 (1964).

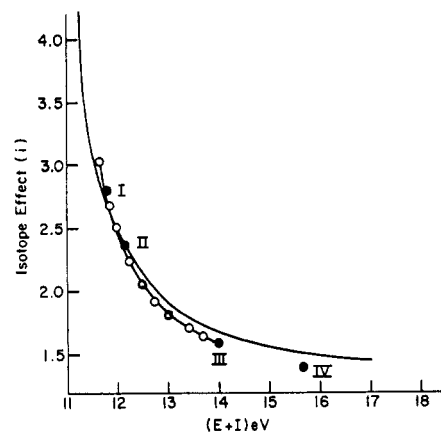


Figure 1. Theoretical variation of the isotope effect with internal energy⁵ (continuous curve) together with i values for toluene molecular ions fragmenting in the source (O) and i values for energy regions I-IV.

have been observed in closely related processes and with change of internal energy.^{5-7,20} Most detailed studies of isotope effects in organic ions have been limited to small molecules.^{6,7} Thus the toluene and cycloheptatriene systems provide suitable models for study.

The improved form of the quasi-equilibrium theory (QET) of mass spectra which employs an exact enumeration of states has recently been applied to fragmentations from large organic molecules,^{5,21} and the toluene system should provide a further sensitive test for the application of this theory to a relatively large molecule. Vestal and Lerner⁵ have calculated the primary isotope effect as a function of internal energy for the loss of H from the toluene ion²² (see Figure 1). By employing the techniques discussed in ref 8 it should be possible to measure the isotope effect in the toluene system over a wide energy range for comparison with the calculated curve.

There are, therefore, two factors operating (scrambling *vs.* direct cleavage and isotope effect) to influence the relative losses of H and D from the toluene and cycloheptatriene ions. To separate the two factors the fragmentations of at least two complementary deuterated species must be investigated. Determinations are reported on the degree of scrambling and isotope effects as a function of the internal energy of the molecular ion—and hence of its lifetime.

Results

Toluene will be considered first; Figure 2 defines the energy segments⁹ (I-IV) used in the investigation.²⁵ In reality, of course, these segments will overlap.

(20) J. K. MacLeod and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 5182 (1967).

(21) F. W. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, and P. Irving, *ibid.*, **92**, 6867 (1970).

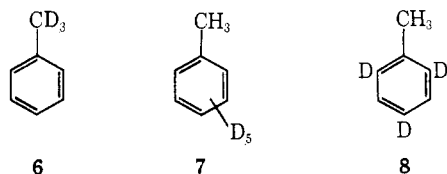
(22) Calculations were based on the assumption that reaction $1 \rightarrow 4$ is the major pathway²³ which is probably incorrect (*vide supra*). However, the parameters (such as molecular vibrational frequencies) and assumptions which would be used for calculations by pathways $2 \rightarrow 5$ or $3 \rightarrow 5$ would be similar to those used for $1 \rightarrow 4$, so similar isotope effects would be predicted.²³ QET calculations have also been made to explain the consecutive metastable peaks in toluene.²⁴

(23) Private communication, M. Vestal, Scientific Research Instruments Corp., Baltimore, Md., April 1970.

(24) L. P. Hills, J. H. Futrell, and A. L. Wahrhaftig, *J. Chem. Phys.*, **51**, 5255 (1969).

(25) The 70 eV $P(E)$ curve is derived from the photoelectron spectrum as described in ref 21. We are indebted to Professor E. Heilbronner for supplying the photoelectron spectra of **1** and **3**.

The deuterated toluenes used are toluene- α - d_3 (6), -ring- d_5 (7), and -2,4,6- d_3 (8). Compounds 6 and 7 are used to calculate isotope effects and degree of scrambling for the energy ranges I-IV and compound 8 is used to confirm these values and to provide a direct contrast with its isomer, 6.



The isotope effect i in the completely scrambled deuterated $C_7H_8^+$ ions is defined for present purposes as the ratio for (loss of H)/(loss of D) corrected for the number of H and D atoms in the ion. For example, the completely scrambled molecular ion of toluene- α - d_3 would yield an H/D ratio of $5i/3$ (it will be assumed that the loss of aryl or vinylic hydrogens is negligible). If the $C_7H_8^+$ ions were monoenergetic, then i would be equal to the kinetic isotope effect k_H/k_D for that energy and could be compared directly to the isotope effects previously calculated for the toluene system.⁵ In practice the i values obtained here for the energy segments I-IV represent the k_H/k_D values averaged over the energy of the particular segment. For the different deuterated toluenes it is reasonable to assume that the energy distributions should be very similar (and hence the i values almost identical) even for the wide energy segments II and III.

Unimolecular Metastable (Energy Region I). The unimolecular metastable abundance ratios (m_H^*/m_D^*) for loss of H and D, respectively, from M^+ are listed for compounds 6-8 in Table I. These are compared with the statistical ratios.

Table I. $[M^+ - H]/[M^+ - D]$ for Unimolecular Metastable Ions from Deuterated Toluenes (70 eV)

	Toluene- α - d_3	Toluene-ring- d_5	Toluene-ring- d_3
m_H^*/m_D^* (unimol)	4.68 ± 0.09	1.68 ± 0.09	4.77 ± 0.15
Observed/statistical	2.81 ± 0.06	2.80 ± 0.15	2.86 ± 0.09

The observed/statistical ratios are the same (within experimental error) for the three compounds. This is consistent with (i) complete H/D scrambling in these low-energy molecular ions and (ii) an isotope effect of 2.8. The calculated^{5,22} isotope effect (Figure 1) is 2.67. The metastable ratios are constant to within a few electron volts of threshold. At 14 eV the ratios are 5.8 ± 0.4 and 2.2 ± 0.3 for compounds 1 and 2 ($i = \sim 3.6$), respectively, and at 13 eV the ratios are 7.3 ± 0.5 and 2.6 ± 0.4 ($i = \sim 4.5$), consistent with the elimination of all ions but those of the lowest internal energy from the metastable "energy window."

Collision-Induced Metastables (Energy Region II). Metastable decompositions from higher energy precursors than the unimolecular metastables may be induced by collision with neutral species (*i.e.*, argon) in the field-free drift region between the ion source and electrostatic sector of a double-focusing mass spec-

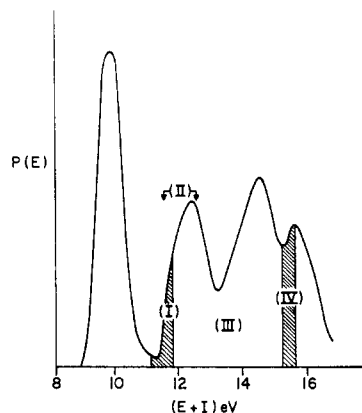


Figure 2. Toluene $P(E)$ curve, illustrating energy segments I-IV.

trometer.²⁶⁻²⁸ The results are shown for compounds 6-8 in Table II. The argon pressure in the first drift region is 2×10^{-4} Torr.

Table II. $[M^+ - H]/[M^+ - D]$ for Collision-Induced Metastable Ions from Deuterated Toluenes (70 eV)

	Toluene- α - d_3	Toluene-ring- d_5	Toluene-ring- d_3
m_H^*/m_D^* (collision)	3.58 ± 0.11	1.44 ± 0.05	3.88 ± 0.09
Observed/statistical	2.15 ± 0.08	2.40 ± 0.08	2.33 ± 0.05

The metastable abundance ratios are all lower than those for the unimolecular metastables, due to decreased isotope effect with increasing energy.⁵ The differences between the observed/statistical ratios for the three compounds indicates a slight preference for loss of α -hydrogen atoms.

Consider the molecular ions that produce collision-induced metastables in the first drift region. Let the isotope effect for these ions be i and the fraction of scrambled ions be α .

For toluene- α - d_3 , the scrambled ions give a metastable ratio (m_H^*/m_D^*) of $5i/3$ and the unscrambled ions give exclusively m_D^* (assuming only loss of α -hydrogens). Therefore the overall expression for the metastable ratio is given by

$$m_H^*/m_D^* = \frac{5i\alpha/(3 + 5i)}{3\alpha/(3 + 5i) + (1 - \alpha)} = 3.58$$

For toluene-ring- d_5 , the scrambled ions give a ratio of $3i/5$ and the unscrambled ions give exclusively m_H^* . Therefore the overall metastable ratio is given by

$$m_H^*/m_D^* = \frac{3i\alpha/(5 + 3i) + (1 - \alpha)}{5\alpha/(5 + 3i)} = 1.44$$

Solution of the simultaneous equations gives values for i and α of 2.33 ± 0.08 and 0.98 ± 0.01 , respectively. These values of i and α predict an m_H^*/m_D^* ratio in toluene-ring- d_3 of 3.97 which agrees well with the observed value of 3.88 ± 0.09 .

(26) W. F. Haddon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 4745 (1968).

(27) F. W. McLafferty and H. D. R. Schudde-mage, *ibid.*, **91**, 1866 (1969).

(28) F. W. McLafferty, I. Howe, R. A. Kornfeld, H. D. R. Schudde-mage, and S.-C. Tsai, in preparation.

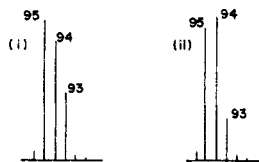


Figure 3. Mass spectra (70 eV) of toluene- α - d_3 (i) and -2,4,6- d_3 (ii) in the molecular ion region.

Thus the isotope effect for collision-induced metastables (2.33) is less than that for the unimolecular metastables (2.80). This is consistent with the increased internal energy of the precursors (after collision) compared with those giving unimolecular metastables. According to the curve shown in Figure 1, a decrease in isotope effect from 2.80 to 2.33 corresponds to the addition of 0.6 eV to the toluene molecular ion.

Since a considerable proportion of toluene molecular ions reaching the first drift region may already be scrambled, the α value calculated for collision-induced metastables (0.98) may not be characteristic of the internal energy of the decomposing ions (*i.e.*, it is a maximum value). Since rearrangement reactions frequently have appearance potentials below those for direct cleavage processes,⁴ it is reasonable to expect that the threshold for hydrogen scrambling in the toluene molecular ion might be below the appearance potential for the loss of hydrogen (11.8 eV).

Daughter Ions Formed in the Source (Energy Region III). The relative proportions of $M^+ - H$ and $M^+ - D$ ions formed in the source at 70/eV from compounds are shown in Table III. Corrections have been

Table III. $[M^+ - H]/[M^+ - D]$ for Normal Daughter Ions from Deuterated Toluenes (70 eV)

	Toluene- α - d_3	Toluene-ring- d_5	Toluene-ring- d_3
$[M^+ - H]/[M^+ - D]$	1.76 ± 0.06	1.14 ± 0.02	2.90 ± 0.04
Observed/statistical	1.06 ± 0.04	1.90 ± 0.03	1.74 ± 0.02

made for ^{13}C and for small percentages of partially deuterated compounds.

It is evident from the observed/statistical ratios that there is a preference for loss of α -hydrogens and the partial spectra (see Figure 3) of isomers 6 and 8 provide a clear indication of this.

Using the values for toluene- α - d_3 and -ring- d_5 in Table III, the following values for i and α are calculated: $i = 1.51 \pm 0.04$, $\alpha = 0.89 \pm 0.01$. Meyer and Harrison¹² report $i = 1.58$.

Again the values for i and α may be used to estimate a value for $[M^+ - H]/[M^+ - D]$ in toluene-ring- d_3 . If 89 % of the M^+ ions give an $[M^+ - H]/[M^+ - D]$ ratio of $5 \times 1.51/3$ and the remaining 11 % give exclusively $M^+ - H$, then the calculated overall ratio is 2.95. This is in excellent agreement with the observed ratio of 2.90 ± 0.04 .

The isotope effect i represents the mean value for ions of energies in region III; the average energy of these ions, weighted according to Figure 2, is 14.0 eV, which corresponds to a calculated isotope effect⁵ of 1.65, in good agreement with the observed value of 1.51 ± 0.04 .

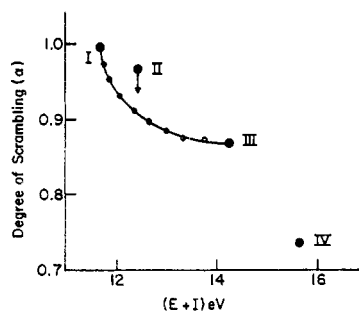


Figure 4. Variation of α with the average energy of toluene molecular ions decomposing in the source (continuous curve) together with α values for energy regions I-IV.

To vary this energy value, the electron beam energy was reduced from 70 eV down to threshold. The energy probability function, $P(E)$, at each electron energy was estimated by application of the linear threshold law to the 70 eV $P(E)$ function (Figure 2), as described in ref 21. For example, it is calculated that electron energies of 16 and 14 eV yield average energy values in energy region III of 12.9 and 12.4 eV, respectively. Figures 1 and 4 show the variation of i and α with the average internal energy of the toluene molecular ions.

M^+ Ions Which Yield Metastable Ions for Loss of Acetylene from " $C_7H_7^+$ " (Energy Region IV). An indirect method may be devised to estimate the relative proportions of deuterated toluene M^+ ions which have sufficient energy both to lose H or D and to decompose further to form $C_5H_5^+$ ions.

The ratio of the sum (Σm_H^*) of the metastables from $C_7H_4D_3^+$ (yielding $C_5H_2D_3^+$, $C_5H_3D_2^+$, and $C_5H_4D^+$) to the sum (Σm_D^*) of those from $C_7H_5D_2^+$ (yielding $C_5H_3D_2^+$, $C_5H_4D^+$, and $C_5H_5^+$) should be nearly equal to the ratio of $C_7H_4D_3^+$ ions to $C_7H_5D_2^+$ ions produced from toluene- α - d_3 M^+ ions of energies just below 15.7 eV by loss of H and D, respectively.⁸ This ratio has been measured for compounds 1-3 at 70 eV and is shown in Table IV.

Table IV. $[M^+ - H]/[M^+ - D]$ from Deuterated Toluenes by the "Indirect Metastable Method"^a

	Toluene- α - d_3	Toluene-ring- d_5	Toluene-ring- d_3
$\Sigma m_H^*/\Sigma m_D^*$	1.01 ± 0.02	1.57 ± 0.03	3.45 ± 0.15
Observed/statistical	0.61 ± 0.01	2.62 ± 0.05	2.07 ± 0.10

^a See ref 9.

The fact that the observed ratio for toluene-ring- d_5 is larger than that for toluene- α - d_3 (although there is a *smaller* proportion of H in the former compound) shows that a significant proportion of decompositions are taking place from the *unscrambled* molecular ion at about 15.7 eV.

The calculation for compounds 6 and 7 gives $i = 1.40 \pm 0.04$ and $\alpha = 0.72 \pm 0.01$. These values of i and α predict a metastable ratio for toluene-ring- d_3 of 3.63, which is close to the 3.45 ± 0.15 observed.

Cycloheptatriene. The relative losses of H and D from two deuterated cycloheptatrienes (9 and 10) have been investigated.

Table V. $[M^+ - H]/[M^+ - D]$ for Deuterated Cycloheptatrienes in Different Energy Regions

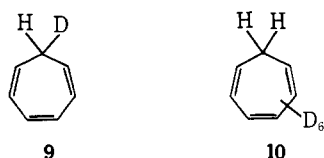
Energy region	Decomposition mode ^a	d_1 (9)	d_6 (10)
I	Unimolecular m^*	17.7 ± 0.4^b (2.53 ± 0.06) ^c	0.89 ± 0.05 (2.67 ± 0.15)
II	Collision-induced m^*	12 ± 1 (1.7 ± 0.2)	0.8 ± 0.1 (2.4 ± 0.3)
III	Daughter ions	7.9 ± 0.2 (1.13 ± 0.03)	0.62 ± 0.02 (1.86 ± 0.06)
IV	Indirect method ^d	5.9 ± 0.1 (0.84 ± 0.02)	0.59 ± 0.01 (1.77 ± 0.03)

^a As described for toluene in Tables I–IV. ^b $[M^+ - H]/[M^+ - D]$ for the particular decomposition mode. ^c Observed/statistical ratios are indicated in parentheses. ^d For the transition $C_7H_7^+ \rightarrow C_6H_6^+ + C_2H_2$ (as for toluene).

Table VI. Values Determined for i and α in Toluene and Cycloheptatriene for Energy Regions I–IV

Region	Av energy, eV ^a	i		α	
		Toluene	CHT	Toluene	CHT
I	11.8	2.80 ± 0.06	2.6 ± 0.1	1.00	0.99 ± 0.01
II	(12.4 ^b)	2.33 ± 0.08	2.1 ± 0.2	0.98 ± 0.01^c	0.95 ± 0.03^c
III	14.0	1.51 ± 0.04	1.49 ± 0.04	0.89 ± 0.01	0.92 ± 0.01
IV	15.7	1.40 ± 0.04	1.22 ± 0.03	0.72 ± 0.01	0.88 ± 0.01

^a Values of $E + I$ for toluene; corresponding values for cycloheptatriene corrected for the heat of formation differences (see text) are 11.8, 12.4, 13.9, and 15.9 eV. ^b Estimated from Figure 1. ^c A maximum value, as scrambling prior to collision is possible.



The 70-eV energy distribution derived for cycloheptatriene²⁵ is shown in Figure 5 and the energy regions I–IV are indicated on the diagram as for toluene. The results for the four energy segments are shown in Table V.

As observed for the toluenes, there is a decrease with increasing energy in the preference for the loss of H from the cycloheptatriene molecular ion. The differences between the values of the observed/statistical ratios found for **9** and **10** illustrate that the scrambling is not complete in energy segments II–IV.

Equations may again be written to determine i and α . For cycloheptatriene- d_1 , the α scrambled ions give $[M^+ - H]/[M^+ - D] = 7i$ and the $(1 - \alpha)$ unscrambled ions give a ratio of i . The overall expression is given by

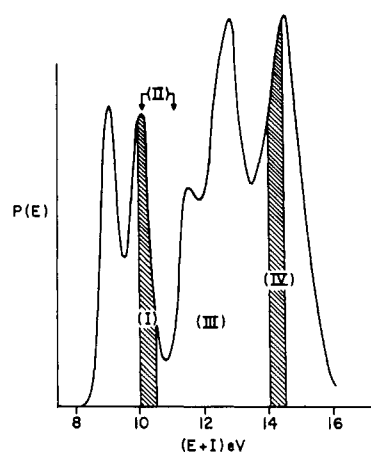
$$[M^+ - H]/[M^+ - D] = \frac{7i\alpha/(7i + 1) + i(1 - \alpha)/(i + 1)}{\alpha/(7i + 1) + (1 - \alpha)/(i + 1)}$$

For cycloheptatriene- d_6 , the α scrambled ions give an H/D ratio of $i/3$ and the $(1 - \alpha)$ unscrambled ions give exclusively loss of H.

$$[M^+ - H]/[M^+ - D] = \frac{i\alpha/(i + 3) + (1 - \alpha)}{3\alpha/(i + 3)}$$

Values for i and α may be determined from these simultaneous equations and the results are shown in Table VI with the toluene values for comparison.

In order that a direct comparison may be made between the cycloheptatriene and toluene systems, a correction must be made because the heat of formation (1.88 eV) of neutral cycloheptatriene is greater than that (0.52 eV) of toluene.¹² For example, only (10.4 + E) eV need be transferred by electron impact to neutral cycloheptatriene to form a $C_7H_8^+$ ion having the same energy (E) and structure as that formed by transfer of (11.8 + E) eV to neutral toluene.

**Figure 5.** Cycloheptatriene $P(E)$ curve, illustrating energy segments I–IV.

Discussion

Isotope Effects. The values calculated⁵ and measured for toluene (Figure 1) show a close resemblance to each other. This strongly supports the use of the quasi-equilibrium theory² to predict the behavior of relatively large organic ions.^{5,20} Although this conclusion is based on the assumption²² that the calculated curve is not particularly sensitive to the structure of the molecular ion, the strikingly similar isotope effects shown by toluene and cycloheptatriene (Table VI) are consistent with mechanisms in which the loss of hydrogen for both occurs from a common intermediate, such as reactions $2 \rightarrow 5$ or $3 \rightarrow 5$. The difference in the values of i for region IV (15.9 eV) appears to be outside experimental error; a possible explanation is that reaction $1 \rightarrow 4^5$ makes a substantial contribution (*vide infra*).

Note that at the lowest energies the isotope effect becomes very large (>4) in comparison to values usually observed in mass spectra. Obviously such effects could seriously compromise the significance of deuterium-labeling studies, especially when it is necessary to use metastables or low bombarding-electron energies to avoid interfering reactions. Complementary labeling,

such as the use of compounds **6**, **7**, and **8** in this study, avoids this difficulty.

The energy value for collision-induced metastables (region II) is, of course, not known *a priori*. The curve in Figure 1 predicts an average energy of 12.4 eV, so that >0.6 eV is added to the molecular ions in the collision process. Note that this is substantially less than that added by electron bombardment, in contrast to previous conclusions.^{27,29}

Degree of Hydrogen Scrambling. The trend observed for α in the results presented in Table VI is a clear indication of competition between a scrambling reaction and a direct cleavage of a C—H bond in the molecular ion. Thus some, if not all, of the decompositions must proceed through pathways that do not involve the symmetrical $C_7H_8^+$ ion, **2**, consistent with the conclusions of Meyer and Harrison.¹²

The rearrangement reaction would be expected to have (i) a tighter activated complex and (ii) a lower activation energy (simultaneous making and breaking of bonds) than the direct cleavage. Under these circumstances the quasi-equilibrium theory predicts²⁻⁴ that the direct cleavage will be favored with increasing internal energies. At the lowest energy at which the direct cleavage rate is fast enough for appreciable reaction in the ion source (*i.e.*, the appearance potential of $C_7H_7^+$, 11.8 eV) the rate of the scrambling reaction is so much higher that most of the decomposing ions are already completely scrambled.

A comparison of the variation of the degree of scrambling α with internal energy in the toluene and cycloheptatriene systems should provide clues for comparing their respective mechanisms of decomposition. Energy regions I and II only give qualitative evidence of similar behavior. For regions III and IV, however, the α values of Table VI show that there is less decomposition taking place from the scrambled $C_7H_8^+$ ions originating from toluene than those from cycloheptatriene. For molecular ions of structure **3** having a particular value of internal energy, the ratio of decompositions taking place from scrambled (**3c**) and unscrambled (**3a**) ions should be *independent* of whether the ions were originally formed directly from cycloheptatriene or from toluene. Hence the lower scrambling values indicate that in high energy toluene ions decompositions are taking place in addition from another unscrambled form of the molecular ion, such as **1a** \rightarrow **4**. Further, any scrambling which accompanies the isomerization **1a** \rightarrow **3a** or which occurs before it, such as **1a** \rightarrow **1b**, must be of small importance in comparison to both this isomerization and to the direct cleavage **1a** \rightarrow **4**.

The α values in region IV provide the greatest contrast. The internal energies of the $C_7H_8^+$ ions in this region are nearly the same for toluene and cycloheptatriene, so that decomposition from ions **3a** and **3c** at that energy should be in the ratio 0.12/0.88 (from the cycloheptatriene data) for both toluene and cycloheptatriene. This ratio can only be maintained in the toluene system if it is assumed that 18% of the decompositions take place from structure **1a**, 10% from **3a**, and 72% from **3c**. These figures retain the same

ion ratio **3a/3c** as in cycloheptatriene and account for the total 28% of decompositions taking place from unscrambled ions at this energy. For ions formed from toluene in energy region III, the relative proportions of decompositions taking place from **1a**, **3a**, and **3c** would be 3, 8, and 89% on the same basis. The increase, with increasing internal energy, in the relative proportion of **1** is wholly consistent with arguments based on the shapes of $k(E)$ curves;²⁻⁴ the isomerization **1a** \rightarrow **3a** requires a tighter activated complex than the direct cleavage of **1a**, so that the relative tendency of the latter should increase with increasing energy. Further, the rate for the direct cleavage of **1a** increases much more rapidly with energy than that for the direct cleavage of **3a**. This is consistent with both a higher activation energy (*vide supra*) and a looser activated complex for hydrogen loss from **1a** vs. that from **3a**.

Scrambling in $C_7H_7^+$ Ions after Formation. The original evidence for both hydrogen¹⁰ and carbon¹⁸ scrambling in the $C_7H_7^+$ ion is based on the isotopic abundances of the secondary $C_6H_5^+$ ions, which are explicable in terms of scrambling either before or during the decomposition $C_7H_7^+ \rightarrow C_6H_5^+$, or both. Our results for the high-energy region IV indicate that 10% of the $C_7H_7^+$ ions are formed by reaction **3a** \rightarrow **5a**, so that for these $C_7H_7^+$ ions the carbon atom originally in the α position could still bear an α -H atom. If the 18% of the $C_7H_8^+$ ions decomposing from **1a** actually form **4**, it is possible that these $C_7H_7^+$ ions have undergone no scrambling. Thus in a substantial proportion of the $C_7H_7^+$ ions formed at higher energies some or all of the carbon and hydrogen atoms could retain the structural relationship to each other that they had in the original toluene molecule.

The metastable decompositions of the $C_7H_7^+$ ions formed from toluene ions of energy region IV can provide information on scrambling of the $C_7H_7^+$ ions *after* formation (before or during decomposition) as well as before or during formation.

These results for toluene- α - d_3 and -ring- d_5 are shown in Table VII; the relative intensities for the three

Table VII. Scrambling in $C_7H_7^+$ Ions

Compd	Precursor	m^*	Transition	Relative abundance	
				Found	Predicted
Toluene- α - d_3	$C_7H_5D_2^+$	48.3	93 \rightarrow 67	10	10
		46.8	93 \rightarrow 66	8.7	10
		45.4	93 \rightarrow 65	0.6	1
	$C_7H_4D_3^+$	49.2	94 \rightarrow 68	7.0	6
		47.8	94 \rightarrow 67	12	12
Toluene-ring- d_5	$C_7H_3D_4^+$	46.3	94 \rightarrow 66	2.8	3
		50.1	95 \rightarrow 69	5.4	6
		48.7	95 \rightarrow 68	12	12
	$C_7H_2D_5^+$	47.3	95 \rightarrow 67	4.8	3
		51.0	96 \rightarrow 70	1.0	1
		49.6	96 \rightarrow 69	10	10
		48.2	96 \rightarrow 68	8.8	10

possible metastables for acetylene loss from a given $C_7H_7^+$ ion are compared to the statistical ratio expected for complete scrambling.

Thus although a significant proportion of the $C_7H_7^+$ ions originating from energy region IV is formed without scrambling, these same ions must then scramble

(29) Although this also appears to be true for other molecular ions, in particular cases fragment ions of higher internal energy can be produced by collisional excitation.^{27,28}

relatively rapidly by isomerization or during decomposition to form $C_5H_5^+$.

It would obviously be of interest to be able to obtain data at higher energies (shorter lifetimes) in order to reduce or even eliminate such scrambling reactions. Meyerson has pointed out that doubly charged toluene molecular ions exhibit a much lower degree of scrambling on decomposition,¹¹ which is consistent with their high ionization potential (24.5 eV).¹⁵ Field ionization offers a method to study ions of very short lifetimes.

Experimental Section

All of the data were determined on a Hitachi RMU-7 double-focusing mass spectrometer. Abundance values were measured with a "bright" ion source, Model MS-101, with 70 eV electron energy (unless otherwise stated), 100 μ A total electron emission current, 185° sample reservoir system, and ion source thermocouple reading of 180°. Measurements in the field-free drift region between the ion source and the electrostatic analyzer were made using the Barber-Elliott-Major defocusing technique.³⁰ All the abundance ratios for which an error is quoted represent the average of

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ten separate values and the quoted error is the standard deviation. All abundances are corrected for ^{13}C . Appearance potentials were determined using the semilogarithmic plot method³¹ with Ar and Xe as standards. For collision-induced metastable measurements, the argon pressure in the first drift region was 2×10^{-4} Torr.

Toluene- α - d_3 (6) and -ring- d_5 (7) were commercial samples of greater than 98.5% isotopic purity. 2,4,6-Trideuteriotoluene (8) was prepared from *m*-toluidine by exchanging the hydrochloride with deuterium oxide in a sealed tube,³² followed by reduction of *m*-toluidinediazonium- d_3 salt with alkaline formaldehyde.³³ The 2,4,6-trideuteriotoluene so formed possessed an isotopic purity (confirmed by low-voltage mass spectrometry) of d_3 , 96.5%; d_2 , 2.6%; d_1 , 0.9%.

Cycloheptatriene-7- d_1 (9)³⁴ was found to have an isotopic content of d_1 , 94.4%. For cycloheptatriene-1,2,3,4,5,6- d_6 (10)³⁴ the isotopic content was d_6 , 96.6%; d_5 , 3.4%.

Acknowledgments. We are grateful to the Army Research Office (Durham) and to the National Institutes of Health (GM-16609) for generous financial support.

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Electron Impact Induced Rearrangements in Isoprenoids¹

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Abstract: Several isoprenyl ketones in which the first isoprene unit is saturated were synthesized and their mass spectra were examined. Due to extensive hydrogen migration, double bond mobility was observed, indicating the limitations of mass spectrometry for detection of the position of a saturated isoprene unit in polyisoprenoids. Corresponding hydrocarbons and alcohols also show hydrogen migration and double bond lability upon electron impact.

Recently mass spectrometry has been used extensively in structural studies of various naturally occurring isoprenoids which contain one saturated unit.²⁻⁴ For example, a C_{43} -isoprenoid ketone containing one saturated unit has been isolated from tubercle bacilli, and from mass spectral data it was concluded that the saturated isoprene unit was the third one from the keto group.³ A similar C_{43} ketone (I) was isolated² from the photooxygenation of the naphthoquinone of *M. phlei*, MK-9 (II, H_2). Low-resolution mass spectral data (Table I) for this compound established that the fragmentation pattern was very similar to that reported³ for the C_{43} ketone from tubercle bacillus. However, there appeared to be a discrepancy in the assignment of the position of the saturated unit.

Table I. Partial Mass Spectrum of C_{43} Ketone (I) Resulting from Photooxygenation of MK-9 (II, H_2)

—M — (69 + 68n)— series			—(69 + 68n)— series		
<i>m/e</i>	<i>n</i>	Rel abundance	<i>m/e</i>	<i>n</i>	Rel abundance
604		3.5	409	5	0.9
535	0	1.0	341	4	1.0
467	1	2.0	273	3	1.2
399	2	2.4	205	2	1.7
331	3	1.4	137	1	23
263	4	5.0	69	0	100
195	5	0			

The main fragmentation pattern in the high mass region for this type of polyisoprenoid compound reflects the successive loss of units of mass 68, due to diallylic cleavage, resulting in a series of peaks of *m/e* [M — (69 + 68n)] for *n* = 0–4, together with two minor series resulting from *m/e* [M — (15 + 68n)] and [M — (43 + 68n)]. Another important but less prominent series, *m/e* (69 + 68n) for *n* = 0–5, also is observed. The absence of a peak at *m/e* 195, due to diallylic

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