Hidden Rearrangements in the Mass Spectral Decomposition of Cycloheptatriene

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Observations concerning the mass spectral decompositions of the toluene and cycloheptatriene molecular ions are reviewed. A mechanism is proposed which explains in a unified manner the apparently conflicting and unresolved isotopic scrambling results. QET calculations supporting this mechanism are presented.

Numerous mass spectral reactions of organic compounds have been shown to involve rearrangement of the carbon skeleton. Few reactions are more unusual and have had more attention directed towards the elucidation of their mechanisms than the formation and decomposition of the $C_7H_7^+$ ion formed from toluene[1]. Extensive D labeling studies have shown that the label is essentially completely scrambled within the decomposing $C_7H_7^+$ ion on the normal ion (10^{-6} sec ion lifetime) time scale. Indeed, toluene-2,6-$^{13}C_2$ shows convincing evidence that nonadjacent labels have become statistically scrambled in forming the $C_5H_5^+$ ion[2]. No explanation has been offered for this unusual result. Labeling studies have also been directed at this mechanistic and structural problem utilizing other C_7H_8 isomers. For example, Meyerson[3a] has found that H/D scrambling is essentially complete in 7-deuterocycloheptatriene within decomposing molecular ions. Most recently, Skell[3b] has found that ^{13}C labels in $^{13}C_2$-cycloheptatriene have become statistically distributed within the $C_5H_5^+$ ion, regardless of the original position of the label. Norbornadiene-$^{13}C_2$ undergoes an electron impact induced Retro Diels-Alder reaction without evidence of skeletal scrambling.

We have also been interested in the timing and mechanism of the decomposition reactions of these isomers and have utilized other approaches. Thus, utilizing ICR techniques[4], toluene molecular ion was shown to undergo reactions typical of aromatic systems, while cycloheptatriene and norbornadiene molecular ions are inert under the same circumstances. From this approach, we may conclude that equilibration of structure does not take place within non-decomposing molecular ions on a time scale significantly longer than that required for mass spectral analysis. Ion kinetic energy[5] studies of toluene and cycloheptatriene have provided information about decomposing molecular ions [Equation (1)] and decomposing $C_7H_7^+$ ions [Equation (2)].

$$C_7H_8^{+\cdot} \rightarrow C_7H_7^+ + H\cdot\,, \qquad (1)$$

$$C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2\,. \qquad (2)$$

Similar amounts of kinetic energy were found to be released from both cycloheptatriene and toluene in both reactions.

We wish to report here on a further approach, and also summarize the evidence in the literature which leads to a unified decomposition mechanism for cycloheptatriene and toluene.

Our desire to test the limitations and applicability of a simplified formulation of quasi-equilibrium theory (QET) to problems of ion structure in general, and to the timing of the equilibration of structure within $C_7H_8^{+\cdot}$ isomers in particular has led to an examination of the mass spectral characteristics of cycloheptatriene and toluene.

Previous studies using the simplified formulation of QET have focused on the determination of the pre-exponential factor A in Eq. (3) as a

$$k(E) = A\,[\,(E - E_0/E]^n \qquad (3)$$

function of substituent in a series of similar compounds[6, 7]. Two approaches have been utilized in the application of this equation. Either n, an effective number of oscillators may be assumed by the best fit for values of the pre-exponential term A and the energy terms E and E_0, respectively, the internal energy of the reacting ion and the activation energy for the process[7], or alternatively, one may assign a value to n and observe changes in the value of A. We have chosen the latter course, and have set a

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value for n by dividing the total degrees of freedom by a factor of three.

Experimental

Commercial samples of toluene and cycloheptatriene were purified by vpc prior to use. Mass spectra were obtained on both Hitachi RMU-6E and AEI MS9 mass spectrometers with source and inlet temperatures at about 80 °C.

Calculations

The calculations were similar to those performed by Benezra and Bursey [6a] with one exception. The energy function for the decomposition of toluene was taken to be $f(E) = \alpha E^{1/2}(E_{\max} - E)$, while that for cycloheptatriene was taken to be $f(E) = \alpha E^{3/2}(E_{\max} - E)$. This was done to partially compensate for the differences in the photoelectron spectra of these compounds [8, *].

Results and Discussion

Ionization and appearance potentials for the major decomposition processes of the molecular ion of toluene and cycloheptatriene at low electron beam energies are given in Table 1.

Table 1. Ionization and appearance potentials.

	Toluene	Cycloheptatriene
IP	8.81	8.52
AP(M−H)	11.8	10.73
AP(M−CH_3)	13.70	14.17

These values were then used to calculate spectral characteristics between 16 and 20 eV, as previously discussed [6b]. The results of these calculations for the M − H reaction are presented in Table 2.

Table 2. Observed and calculated ratios of $[M-H]^+/M^{+\cdot}$ in Toluene and Cycloheptatriene [a].

	Toluene			Cycloheptatriene		
eV	obs	calc	$A_{\mathrm{sec}^{-1}}$	obs	calc	$A_{\mathrm{sec}^{-1}}$
14	.103	.103	7×10^7	.320	.367	2×10^7
16	.200	.194	6×10^7	.490	.472	2×10^7
18	.310	.320	6×10^7	.650	.603	1×10^7
19	.420	.455	6×10^7	.835	.871	1×10^7
20	.520	.524	5×10^7	.954	.962	8×10^6

[a] The calculated ratios and values for A are based upon the literature A.P. and I.P. values. Similar results were also obtained using a combination of our A.P. and I.P. results with literature value for the (M−CH_3) reaction.

The values for the pre-exponential factor (columns 4 and 7) are quite similar, and based upon previously made observations [6, 7] indicate that in both cycloheptatriene and toluene, the loss of a hydrogen involves a rearrangement. This result from the simplified QET calculations is not entirely unexpected, as deuterium labeling studies have shown essentially statistical loss of H and D prior to the formation of the $C_7H_7^+$ ion [3a].

We now address ourselves to the mechanistic and structural problem associated with the fact that loss of hydrogen from cycloheptatriene molecular ion involves a rearrangement reaction which appears to be as extensive as the structural reorganization involved in the decomposition of toluene molecular ion. The structural rearrangement involved in the M − H reaction is, it should be noted, unrelated to the presence or absence of various isotopic labels. It is only by use of these labels that previous workers were able to observe these phenomena. Although numerous H/D scrambling mechanisms may be written, the rate determining step for the *loss of hydrogen* ($A \sim 10^8$) cannot occur from skeletally unrearranged molecular ions unless the H/D scrambling (hydrogen rearrangement) mechanism has a rate greater than that of a simple bond cleavage [**].

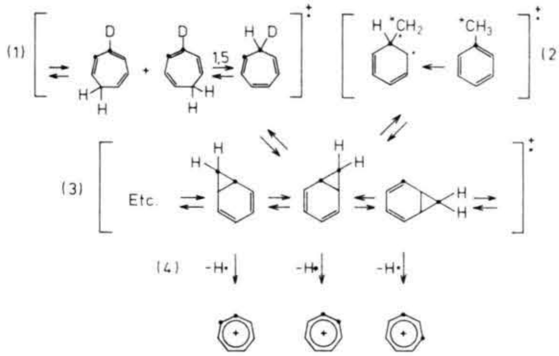

Fig. 1. (1) 1,5 sigmatropic rearrangement to scramble hydrogen in cycloheptatriene. (2) Entrance of toluene into scrambling mechanism (cf. Ref. 1b). (3) Scrambling of carbon atoms through 1,5 sigmatropic rearrangements involving norcaradienes. (4) Formation of completely scrambled (C and H) tropylium ions. Loss of hydrogen with simultaneous concerted ring opening of norcaradiene is the rate determining step.

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[*] When the same energy function was used to make the calculation, small differences in the frequency factor (A) as a function of voltage were obtained. The values of A for cycloheptatriene were increased by about a factor of five.

[**] Simple bond cleavages should have A factors of about $10^{12}-10^{13}$ sec^{-1} [6, 7].

Thus, if the H/D scrambling were fast enough to compete with an apparent simple cleavage of hydrogen, then the scrambling mechanism cannot be responsible for the low A factor found by our QET calculations. For example, H/D scrambling in 7-deuterocycloheptatriene upon electron impact may be visualized as taking place either through 1,5-thermally allowed or 1,3-photochemically allowed sigmatropic rearrangements. Neither of these processes are sufficient to account for the observed QET results as the same rearrangement processes may be visualized as also occurring in undeuterated cycloheptatriene. In the absence of deuterium labeling, the hydrogen rearrangement process becomes degenerate, and in itself cannot be responsibe for the QET prediction that the loss of hydrogen reaction involves rearrangement.

We are thus faced with the paradoxical situation of observing (by use of deuterium labeling) a rearrangement process which cannot be the rate determining step. The recent ^{13}C-labeling studies on cycloheptatriene by Skell confirm our earlier prediction[10] concerning the scrambling of carbon atoms prior to formation of the $C_5H_5^+$ ion. Indeed these results, in conjunction with those of Siegel[2] provide the key to a unified decomposition mechanism of a toluene and cycloheptatriene.

A mechanistic picture of the primary decomposition pathways of toluene has been presented by McLafferty[8, 11]. This picture does not take into full account the relationship of cycloheptatriene, nor does it explain the presence of the degenerate rearrangement of the available ^{13}C results. An alternative view, consistent with the previously known information is shown in the Figure 1. For cycloheptatriene, hydrogen/deuterium scrambling (1) is pictured as occurring via 1,5 sigmatropic rearrangements; closure across carbons 1 and 6 produce a series of norcaradienes which interconvert through a series of 1,5 carbon shifts (2), followed by loss of hydrogen concomitant with ring opening (3) to form a skeletal and proton-scrambled cycloheptatriene, which upon further decomposition leads to the ^{13}C results found by Skell. Proton and carbon-13 scrambling within toluene may likewise be explained on the basis of thermally allowed sigmatropic rearrangements. Following transfer of an α-hydrogen to C_1 (4), closure between $C_\alpha$and C_2 (or C_6) produces a series of norcaradienes (5). "Leakage" from the norcaradienes to cycloheptatriene to allow H/D scrambling (2), return to the interconverting norcaradienes, followed by loss of hydrogen and ring opening will produce an almost statistically H/D scrambled tropylium ion, as well as, upon further decomposition, the ^{13}C results found by both Rinehart and Siegel. The last step – concerted ring opening concomitant with loss of H(D) – is viewed as the rate determining step in the formation of the $C_7H_7^+$ ion.

The principal features of this mechanism are:

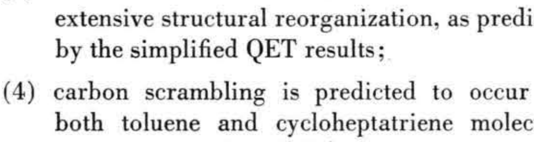
(1) the non-equilibration of non-reactive molecular ions, consistent with the ICR results[4];

(2) the equilibration of structure between the cycloheptatriene and toluene systems within decomposing molecular ions, prior to loss of hydrogen, in agreement with the IKES results[5];

(3) the observation that the M – H reaction involves extensive structural reorganization, as predicted by the simplified QET results;

(4) carbon scrambling is predicted to occur for both toluene and cycloheptatriene molecular ions as observed in $C_5H_5^+$ ions.

We also wish to call attention to the transannular hydrogen migration mechanism within the cycloheptatriene molecular ion. For this to occur, the molecular geometry, as in the analogous ground state reaction, must be in a nonplanar configuration [Eq. (4)]. From this conformation, closure between C_1 and C_6 forming a norcaradiene would also be possible. In fact, the activation energy for this process in the neutral molecule is estimated to be less endothermic[12] (18 kcal/mole)



(4)

than that for the transannular hydrogen transfer (31 kcal/mole)[13], or the skeletal rearrangement (50 kcal/mole) involved in the formation of toluene from cycloheptatriene[14].

We thus find that the decompositions of cycloheptatriene and toluene may be viewed as a unified process, may be accounted for in terms of conventional sigmatropic and electrocyclic reactions, and are consistent with the predictions of simplified quasi-equilibrium theory. Further studies involving stable norcaradienes are in progress and will be presented later.

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[1] (a) P. N. Rylander, S. Meyerson, and H. M. Grubb, J. Amer. Chem. Soc. **79,** 842 [1957]; (b) H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organis Ions", F. W. McLafferty, ed., Academic Press, New York (N. Y.) 1963, p. 453; (c) S. Meyerson, Rec. Chem. Progr. **26**, 257 [1965]; (d) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, J. Amer. Chem. Soc. **90**, 2983 [1968].

[2] A. S. Siegel, ibid. **92,** 5277 [1970].

[3] (a) S. Meyerson, ibid. **85,** 3340 [1963]; (b) C. Davidson and P. S. Skell, ibid. **95**, 6843 [1973].

[4] M. K. Hoffman and M. M. Bursey, Tetrahedron Lett. **1971**, 2539.

[5] R. G. Cooks, M. Bertrand, J. H. Beynon, and M. K. Hoffman, Org. Mass Spectrom. **7**, 1303 [1973].

[6] (a) S. A. Benezra and M. M. Bursey, J. Chem. Soc. (B) **1971,** 1515; (b) S. A. Benezra and M. M. Bursey, Z. Naturforsch. **27 a**, 670 [1972].

[7] (a) A. N. H. Yeo and D. H. Williams, J. Amer. Chem. Soc. **92**, 3984 [1970]; (b) A. N. H. Yeo and D. H. Williams, Chem. Commun. **1969**, 956; (c) I. Howe and D. H. Williams, J. Amer. Chem. Soc. **91,** 7137 [1961].

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

[9] (a) J. G. Dillard, K. Draxl, J. L. Franklin, F. H. Field, J. T. Herron, and H. M. Rosenstock, NSRDS-NBS 26, Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions, U. S. Department of Commerce, 1969; (b) R. J. Kendel, J. Chem. Phys. **22,** 1496 [1954].

[10] M. K. Hoffman, Abstracts, XXIII IUPAC Meeting, Boston, July 2, 1971.

[11] K. Levsen, F. W. McLafferty, and D. M. Jerina, J. Amer. Chem. Soc. **95**, 6332 [1973].

[12] J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, ibid. **89,** 4076 [1967].

[13] A. P. TerBorg, H. Kloosterziel, and N. Van Meurs, Rec. Trav. Chim. **83,** 717 [1963]; Proc. Chem. Soc. **1962**, 359.

[14] W. G. Woods, J. Org. Chem. **23,** 110 [1958].