structure of the reference substrate (for the compounds studied here, benzene), of the reagent, and so on. In order to estimate the relations between the interaction constant q and the reaction parameters such as the electrophilicity of the reactant, the charge of the transition state, etc., a large set of electrophilic substitution reactions should be used. For this reason, research is in progress to obtain new values for the electrophilic substitution reactions of polysubstituted compounds.

Rearrangement of the Benzene Molecular Ion on Electron-Impact Ionization

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Abstract: The scrambling processes which take place after electron-impact ionization of benzene have been studied using the isotopically labeled compound benzene-*1,2*-$^{13}C_2$-*3,4,5,6*-d_4. The abundances of the various isotopic neutral fragments of C_2H_2 and $C_3H_3\cdot$ which are lost from this molecular ion were measured. The experimental results were then compared to sets of several theoretical results derived from calculations which assumed the occurrence of various scrambling processes. This comparison, when taken with experimental data derived from processes occurring in the ionization chamber, showed predominantly that total randomization of carbons and hydrogens had occurred, although a moderate contribution of the process involving only hydrogen scrambling could not be ruled out. However, when metastable ions were studied, ions with much longer lifetimes were involved; the results in this case showed that total randomization had occurred.

Electron bombardment ionization of an organic molecule in a mass spectrometer may lead to an exchange or scrambling of atoms within an ion. Recent work with isotopically substituted[1,2] and unsubstituted[3] benzene, benzylic ions,[4,5] thiophenes,[6] and other aromatic and heteroaromatic compounds[7] shows that there is major scrambling of the carbon skeleton and of the hydrogens in the molecular ion of these compounds. Benzene is of particular interest in this regard because it is a symmetrical aromatic molecule and thus the scrambling process may be observed unhindered by the complicating effects of various groups substituted on the ring. In the mass spectrum of benzene, the molecular ion loses $H\cdot$, H_2, C_2H_2, $C_3H_3\cdot$, and $CH_3\cdot$, to yield, respectively, $C_6H_5^+$, $C_6H_4\cdot^+$, $C_4H_4\cdot^+$, $C_3H_3^+$, and $C_5H_3^+$. When these losses were studied in various deuterated benzenes, the data suggested that the hydrogens had become randomized as to position on the ring.[8,9] Of course, this phenomenon was not totally unexpected, since, in the loss of $CH_3\cdot$, a major rearrangement of the molecule must take place. Also, interconversion and rearomatization of Dewar benzenes, prismanes, and benzvalenes are known to occur thermally and photochemically, giving rise to scrambling of the carbon skeleton.

These considerations lead to the question: to just what extent do the individual atoms rearrange within this simple molecule? If the carbon atoms randomize to a large extent, do they carry their original hydrogen atoms along or are these hydrogens themselves also scrambling? Thus, for the molecular ion of benzene, one or more of the following mechanisms may operate: case 1, no randomization; case 2, randomization of carbon atoms only (each carbon carries along its original hydrogen); case 3, randomization of hydrogen only (carbon skeleton stable); case 4, total atomic randomization. It is possible to deduce the relative importance of these cases by the study of the isotopic composition of the neutral fragment lost from a particular isotopically substituted benzene molecular ion. The loss of fragments such as C_2H_2 and $C_3H_3\cdot$ does not necessitate *a priori* a rearrangement, as in the case of loss of $CH_3\cdot$, so that no studies on loss of the former fragments are possible without isotopic labeling. Such a study was done by measuring first the abundance of the various isotopic species in the mass spectrum for loss of "C_2H_2" and "$C_3H_3\cdot$" using high-resolution mass spectrometry. (The symbolism used throughout this paper is that quotation marks mean the inclusion of all isotopic species.) This gives a measure of the extent of the possible scrambling processes occurring within the ionization chamber.

The decompositions of metastable molecular ions of labeled benzene resulting in loss of "C_2H_2" and "$C_3H_3\cdot$" were also studied. Metastable ions decompose in a time of the order of 10^{-5} sec after ionization, while the stable ions normally seen in a mass spectrum arise

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(1) C. G. McDonald and J. Shannon, *Aust. J. Chem.*, 15, 771 (1962).

(2) I. Horman, A. N. H. Yeo, and D. H. Williams, *J. Amer. Chem. Soc.*, 92, 2131 (1970); R. J. Dickinson and D. H. Williams, *J. Chem. Soc. B*, 249 (1971).

(3) R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, 87, 4653 (1965).

(4) 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.

(5) S. Meyerson, H. Hart, and L. C. Leitch, *J. Amer. Chem. Soc.*, 90, 3419 (1968).

(6) D. H. Williams, R. G. Cooks, J. Ronayne, and S. W. Tam, *Tetrahedron Lett.*, 1777 (1968).

(7) D. H. Williams, S. W. Tam, and R. G. Cooks, *J. Amer. Chem. Soc.*, 90, 2150 (1968).

(8) K. R. Jennings, *Z. Naturforsch. A*, 22, 454 (1967).

(9) M. A. Baldwin, D. P. Craig, and A. Maccoll, ASTM Committee E-14, 17th Annual Conference on Mass Spectroscopy and Allied Topics, Dallas, Tex., 1969.

from very much faster processes, taking place on the order of 10^{-7} sec. We could thus expect that if scrambling of the atoms in benzene does occur but that it does not go to completion within the ionization chamber, as previous data have shown, then more complete scrambling should be observed in decompositions of these longer lived ions. To record these metastable ion decompositions, the techniques of ion kinetic energy spectroscopy (ikes) and HV (high voltage) scanning were employed using a double-focusing mass spectrometer.[10,11] In both cases, the results were compared with a theoretical set of results derived by considering all possible structures which can occur in the four cases given above and the probability of loss of "C_2H_2" or "$C_3H_3\cdot$" from each possible structure. A preliminary report of that portion of the work concerned with the high-resolution measurements has been published.[12]

Experimental Section

All spectra were obtained on a Hitachi Perkin-Elmer RMH-2 double-focusing mass spectrometer[10] at an ionizing voltage of 70 eV, and, for the mass spectra, at an accelerating voltage of 9.6 kV, a total filament emission of 1 mA, and a resolution of 25,000 at 5% valley. The sample pressure was maintained at 2.0–2.5 × 10^{-6} Torr. The resolution was kept to a minimum to provide best sensitivity; measurements were made at slow scan speeds in the mass regions of interest to get reproducible peak heights. Intensities are expressed as an average of at least six measurements, and show an experimental average deviation of ±4%. For simplicity, the most intense ion in both the "C_2H_2" and "$C_3H_3\cdot$" ion cluster was taken as the base peak in that cluster for measurements of peak intensities.

Results

Theoretical. The method used to compute the theoretical results based on statistical considerations is given in the following paragraphs. Isotope effects have been neglected in these calculations since these should be small, particularly in cases with simultaneous bond cleavage and bond formation.

The general approach to these calculations involves the determination of several factors. First, the percentage labeling of ^{13}C and D must be measured using high-resolution techniques. It was found that the percentage deuteration was high, with the benzene-d_4 species constituting 93.2% of the total deuterated species and -d_3, 6.8%. The abundances of the d_2, d_1, and d_0 species were negligible. For ^{13}C, it was found that the $^{13}C_2$ species made up 32.3% of the total species labeled with this isotope, $^{13}C_1$, 49.3%, and $^{13}C_0$, 18.5%. The combined isotopic make-up of the sample is given in Table I. The occurrence of ^{13}C and D at their natural abundances has been allowed for in these calculations.

The second step in deriving the theoretical peak heights to be expected for the various scrambling processes or cases given earlier involves the determination of the structures of all the molecular ions possible in keeping with the conditions involved for each case. Often, degeneracy of structure occurs, giving rise to a structural factor. This factor is merely a fraction relating the number of times a specific structure occurs to the total number of structures. Third, the number of ways of losing "C_2H_2" and "$C_3H_3\cdot$" for each structure in each case must be calculated. This simply involves inspection of a structure and determination of the probability of loss of a certain species, giving rise to a probability factor for that structure. The probability of loss of a given isotopic species is obtained by multiplying the structural factor by the probability factor for each structure and summing over all structures. It is then only necessary to multiply this value by the fraction of each specific isotopic molecular ion present in the sample and to sum over all molecular species to give the final value for the probability of loss of a given isotopic fragment. These points will be illustrated in the following paragraphs.

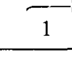
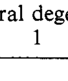
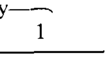
Table I. Isotopic Composition of the Molecular Ions of Labeled Benzene

m/e	Isotopic species present	Rel abundance, %
84	$^{13}C_2$, D_4	29.8
83	$^{13}C_2$, D_3	2.5
	$^{13}C_1$, D_4	45.8
82	$^{13}C_1$, D_3	3.5
	$^{13}C_0$, D_4	17.6
81	$^{13}C_0$, D_3	0.9

The data giving the final results for each case are presented in Tables II–V. To simplify the presentation, the positions of the labels for the structures considered are indicated on the carbon skeleton as a circle for ^{13}C and a dot for D. The structural factor, or degeneracy of a given structure, is given below the structure as a fraction. To further aid in this description, only the tetradeuterated molecular ion species containing zero, one, and two ^{13}C atoms is considered here, although the D_3 species were taken into account in deriving the final theoretical results. Let us now consider the individual cases.

Case 1. No Randomization. In deducing the possible ions and their relative abundances, it was necessary to consider only the three structures given in Table II and the possible isotopic species that would result

Table II. Probability of Loss of "C_2H_2" and "$C_3H_3\cdot$" for Case 1

	Molecular species		
	$^{13}C_2D_4$	$^{13}C_1D_4$	$^{13}C_0D_4$
	Structures[a]		
			
	Structural degeneracy		
Neutral fragment lost	1	1	1
"C_2H_2"			
$^{13}C_2H_2$	1	–	–
$^{13}CCHD$	2	1	–
$^{13}CCH_2$	–	1	–
C_2H_2	–	–	1
C_2HD	–	1	2
C_2D_2	3	3	3
"$C_3H_3\cdot$"			
$^{13}C_2CH_2D\cdot$	2	–	–
$^{13}CC_2HD_2\cdot$	2	1	–
$^{13}CC_2H_2D\cdot$	–	2	–
$C_3H_2D\cdot$	–	–	2
$C_3HD_2\cdot$	–	1	2
$C_3D_3\cdot$	2	2	2

[a] Open circles denote the positions of ^{13}C, solid circles the positions of D.

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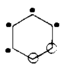
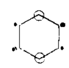
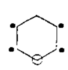
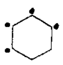
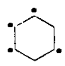
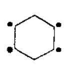
(10) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Int. J. Mass Spectrom. Ion Phys.*, 3, 313 (1969).

(11) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, 3, 455 (1970).

(12) W. O. Perry, J. H. Beynon, W. E. Baitinger, J. W. Amy, R. M. Caprioli, R. N. Renaud, L. C. Leitch, and S. Meyerson, *J. Amer. Chem. Soc.*, 92, 7236 (1970).

Table III. Probability of Loss of "C_2H_2" and "$C_3H_3\cdot$" for Case 2

	$^{13}C_2D_4$[a]			$^{13}C_1D_4$[a]			$^{13}C_0D_4$[a]		
	Structures								
									
Neutral fragment lost	2/5	2/5	1/5	2/5	2/5	1/5	2/5	2/5	1/5
"C_2H_2"									
$^{13}C_2H_2$	1	–	–	–	–	–	–	–	–
$^{13}CCHD$	2	4	4	1	2	2	–	–	–
$^{13}CCH_2$	–	–	–	1	–	–	–	–	–
C_2H_2	–	–	–	–	–	–	1	–	–
C_2HD	–	–	–	1	2	2	2	4	4
C_2D_2	3	2	2	3	2	2	3	2	2
"$C_3H_3\cdot$"									
$^{13}C_2CH_2D\cdot$	2	–	–	1	–	–	–	–	–
$^{13}CC_2HD_2\cdot$	2	1	-	4	2	–	6	3	–
$^{13}CC_2H_2D\cdot$	–	2	–	–	1	–	–	–	–
$C_3H_2D\cdot$	–	–	2	–	–	1	–	–	–
$C_3HD_2\cdot$	–	1	2	–	2	4	–	3	6
$C_3D_3\cdot$	2	2	2	1	1	1	–	–	–

[a] Molecular species. Open circles denote the positions of ^{13}C, solid circles the positions of D. Fractions below structures indicate structural degeneracy.

from the appropriate cleavages. Thus, the $^{13}C_2D_4$ structure can be cleaved in three ways to lose C_2D_2, in two ways to lose $^{13}CCHD$, and in one way to lose $^{13}C_2H_2$. The $^{13}C_1D_4$ species can be cleaved in three ways to lose C_2D_2, one way for $^{13}CCH_2$, one way for $^{13}CCHD$, and one way for C_2HD. Similarly, the $^{13}C_0D_4$ species can be cleaved in three ways to lose C_2D_2, two ways for C_2HD, and one way for C_2H_2. For the loss of "$C_3H_3\cdot$," the $^{13}C_2D_4$ ion can be cleaved in two ways to give $C_3D_3\cdot$, two ways for $^{13}CC_2HD_2\cdot$, and two ways for $^{13}C_2CH_2D\cdot$. The $^{13}C_1D_4$ ion can be cleaved two ways to give $C_3D_3\cdot$, two ways for $^{13}CC_2H_2D\cdot$, one way for $^{13}CC_2HD_2\cdot$, and one way for $C_3HD_2\cdot$. The $^{13}C_0D_4$ ion can be cleaved in two ways to give $C_3D_3\cdot$, two ways for $C_3HD_2\cdot$, and two ways for $C_3H_2D\cdot$. These values, when multiplied by the percentage abundance of the three molecular species in the sample, give the total probability of loss of a given species from a given structure. These data are given in Table II.

Case 2. Randomization of CH Groups in the Ring. In this case, carbon atoms along with their attached hydrogens become randomly distributed around the ring; only C–C bond cleavage and formation occur. There are nine different structures which can be obtained in this manner. These are shown in Table III. However, structural degeneracy does occur in some of these cases, *e.g.*, the 1,2-$^{13}C_2$ molecular species is identical with the 1,5-$^{13}C_2$ species, and so forth. Thus, the structural degeneracy factor gives the number of times the given structure appears out of the total. Table III summarizes the theoretical results calculated for case 2.

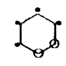
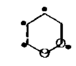
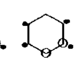
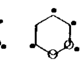
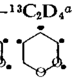
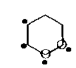
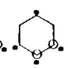
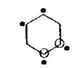
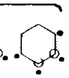
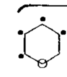
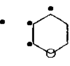
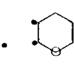
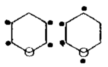
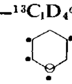
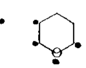
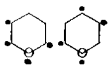
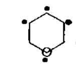
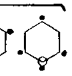
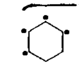
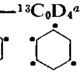
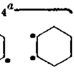
Case 3. Randomization of Hydrogen Only. Scrambling of hydrogen and deuterium occurs on a rigid carbon skeleton in this process. There are nine possible arrangements of H and D on the 1,2-$^{13}C_2$ molecule, nine more arrangements on the $^{13}C_1$ molecule, and three on the $^{13}C_0$ molecule. Again, there is considerable structural degeneracy. The data calculated from case 3 are summarized in Table IV.

Case 4. Complete Randomization of Carbon and Hydrogen. This situation is, of course, the most complex, combining cases 2 and 3. The randomization or scrambling of carbon atoms in the ring and hydrogen atoms on the ring is considered to occur simultaneously. There are 24 different structural arrangements possible for the $^{13}C_2$ molecular species in keeping with the conditions of case 4. These are shown in Table V. There are nine structures for the $^{13}C_1$ molecular species and three for the $^{13}C_0$ species. However, since the structures and probabilities of loss of "C_2H_2" and "$C_3H_3\cdot$" from both these species are identical with those of case 3, the results shown in Table IV are appropriate and will not be repeated here. Thus, we need only consider here the additional structures arising from the $^{13}C_2$ molecular species. The calculated results for these structures are given in Table V.

Experimental. The isotopic composition of the sample was determined by slowly scanning the molecular ion region at high resolution and measuring peak intensities from *m/e* 78 to 84. The calculated contribution of each isotopic species is given in Table I. Corrections have been made for the slight sample pressure variations during the runs and for the presence of naturally occurring ^{13}C.

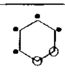
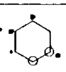
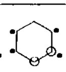
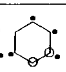
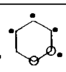
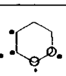
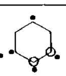
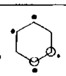
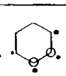
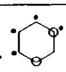
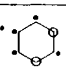
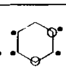
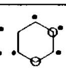
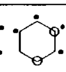
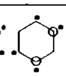
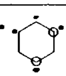
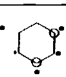
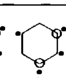
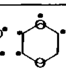
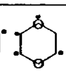
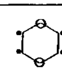
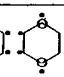
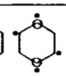
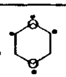
The experimentally determined ion intensities of the various isotopically substituted species measured from the mass spectrum of the labeled benzene sample are given in Table VI. The proper portions of the ike spectra showing loss of "C_2H_2" and "$C_3H_3\cdot$" are given in Figure 1. As seen in these spectra, the overlapping peaks make it very difficult to measure ion intensities with sufficient accuracy for our purpose. For example, the peak at approximately 0.663*E* (where *E* is the energy of the main ion beam) is due to the daughter ions of two decompositions: $83^+ \rightarrow 55^+ + 28$ and $80^+ \rightarrow 53^+ + 27$. Thus, decompositions of the variously labeled molecular ions (and also of fragment ions) can contribute to each peak. However, when HV scans were obtained, the decompositions involving the doubly ^{13}C-labeled molecular ion of *m/e* 84 could be isolated and measured. In Figure 2 are shown the appropriate peaks for the decompositions $84^+ \rightarrow 56^+ + 28$ and $84^+ \rightarrow 57^+ + 27$. While they overlap slightly with the

Table IV. Probability of Loss of “C_2H_2” and “$C_3H_3\cdot$” for Case 3

	$^{13}C_2D_4$[a]									$^{13}C_1D_4$[a]									$^{13}C_0D_4$[a]		
																					
Neutral fragment lost	2/30	4/30	4/30	4/30	4/30	4/30	4/30	2/30	2/30	4/30	4/30	2/30	4/30	4/30	4/30	4/30	2/30	2/30	6/15	6/15	3/15
“C_2H_2”																					
$^{13}C_2H_2$	1	—	—	—		—	—	—	—												
$^{13}C_2HD$	—	1	1	1	1	—	—	—	—												
$^{13}C_2D_2$	—	—	—	—	—	1	1	1	1												
$^{13}CCH_2$	—	—	—	—	1	—	—	—	—	1	—	—	—	—	—	—	2	—			
$^{13}CCHD$	2	2	1	1	—	1	1	2	—	1	2	2	1	1	2	1	—	—			
$^{13}CCD_2$	—	—	1	1	1	1	1	—	2	—	—	—	1	1	—	1	—	2			
C_2H_2	—	—	—	—	—	1	—	—	1	—	—	—	1	—	1	—	—	—	1	—	—
C_2HD	—	1	2	2	1	1	3	2	2	1	2	2	1	3	2	3	2	4	2	4	4
C_2D_2	3	2	1	1	2	1	—	1	—	3	2	2	2	1	1	1	2	—	3	2	2
“$C_3H_3\cdot$”																					
$^{13}C_2CH_2D\cdot$	2	1	2	—	1	—	—	—	—												
$^{13}C_2CHD_2\cdot$	—	1	—	2	1	1	1	2	—												
$^{13}C_2CD_3\cdot$	—	—	—	—	—	1	1	—	2												
$^{13}CC_2H_2D\cdot$	—	—	—	1	1	1	—	—	—	2	1	—	1	—	—	—	1	—			
$^{13}CC_2HD_2\cdot$	2	1	2	—	—	—	2	2	2	1	2	3	1	2	1	3	2	2			
$^{13}CC_2D_3\cdot$	—	—	—	1	1	1	—	—	—	—	—	—	1	1	2	—	—	1			
$C_3H_2D\cdot$	—	—	—	—	—	1	1	—	2	—	—	—	1	1	2	—	—	1	2	1	—
C_3HD_2	—	1	—	2	1	1	1	2	—	1	2	3	1	2	1	3	2	2	2	4	6
C_3D_3	2	1	2	—	1	—	—	—	—	2	1	—	1	—	—	—	1	—	2	1	—

[a] Molecular species. In the structures open circles denote the positions of ^{13}C, solid circles the positions of D. Fractions below structures indicate structural degeneracy.

Table V. Probability of Loss of “C_2H_2” and “$C_3H_3\cdot$” for Case 4[a]

																								
Neutral fragment lost	4	8	8	8	8	8	8	4	4	8	4	8	8	8	4	8	8	4	8	8	2	4	4	4
“C_2H_2”																								
$^{13}C_2H_2$	1	—	—	—	—	—	—	—	—															
$^{13}C_2HD$	—	1	1	1	1	—	—	—	—															
$^{13}C_2D_2$	—	—	—	—	—	1	1	1	1															
$^{13}CCH_2$	—	—	—	—	1	—	—	—	—	1	—	—		1	1	—	—	—	1	—	—	—	—	—
$^{13}CCHD$	2	2	1	1	—	1	1	2	—	2	4	3	2	1	1	2	3	1	1	3	4	2	2	2
$^{13}CCD_2$	—	—	1	1	1	1	1	—	2	1	—	1	2	2	2	2	1	3	2	1	—	2	2	2
C_2H_2	—	—	—	—	—	1	—	—	1	—	—	—	—	—	—	—	—	1	—	—	—	1	—	—
C_2HD	—	1	2	2	1	1	3	2	2	—	—	1	2	1	1	2	1	1	1	1	—	—	2	2
C_2D_2	3	2	1	1	2	1	—	1	—	2	2	1	—	1	1	—	1	—	1	1	2	1	—	—
“$C_3H_3\cdot$”																								
$^{13}C_2CH_2D\cdot$	2	1	—	—	1	—	—	—	—	1	2	—	—	—	—	—	—	—						
$^{13}C_2CHD_2\cdot$	—	1	2	2	1	1	1	2	—	—	—	1	1	1	1	1	1	—						
$^{13}C_2CD_3\cdot$	—	—	—	—	—	1	1	—	2	—	—	—	—	—	—	—	—	1						
$^{13}CC_2H_2D\cdot$	—	—	—	1	1	1	—	—	—	1	—	—	1	2	2	1	—	1	2	1	—	2	—	1
$^{13}CC_2HD_2\cdot$	2	2	2	—	—	—	2	2	2	2	2	4	2	—	—	2	4	2	2	4	6	2	6	4
$^{13}CC_2D_3\cdot$	—	—	—	1	1	1	—	—	—	1	—	—	1	2	2	1	—	1	2	1	—	2	—	1
$C_3H_2D\cdot$	—	—	—	—	—	1	1	—	2		—	—	—	—	—	—	—	1						
$C_3HD_2\cdot$	—	1	2	2	1	1	1	2	—	—	—	1	1	1	1	1	1	—						
C_3D_3	2	1	—	—	1	—	—	—	—	1	2	—	—	—	—	—	—	—						

[a] Molecular species is $^{13}C_2D_4$. In structures open circles denote the position of ^{13}C, solid circles the positions of D. Numbers below structures indicate repetitive structures out of a total of 150, *i.e.*, the structural degeneracy.

Table VI. Comparison of Theoretical and Experimental Data Derived from the Mass Spectra

Case	Loss of "C_2H_2"								
	Isotopic composition of fragment ion								
	$^{13}C_0D_2$	$^{13}C_1D_2$	$^{13}C_0D_3$	$^{13}C_2D_2$	$^{13}C_1D_3$	$^{13}C_0D_4$	$^{13}C_2D_3$	$^{13}C_1D_4$	$^{13}C_2D_4$
	Nominal mass								
	54	55	55	56	56	56	57	57	58
	Experimental relative abundance								
	13.2	20.5	17.4	7.4	27.2	2.7	7.3	3.3	1.0
	Deviation								
	±0.2	±0.5	±0.5	±0.1	±0.4	±0.3	±0.2	±0.2	±0.1
	Theoretical relative abundances for "$C_4H_4\cdot^+$," loss of "C_2H_2"								
1	9.8	25.1	15.0	15.8	18.4	15.9	0	0	0
2	8.3	21.1	22.8	12.6	28.9	6.3	0	0	0
3	16.5	18.0	20.6	6.7	22.6	2.7	8.3	3.2	1.4
4	15.1	20.8	18.9	5.3	25.9	2.5	6.7	3.7	1.1

Case	Loss of "C_3H_3"								
	Isotopic composition of fragment ion								
	$^{13}C_0D_1$	$^{13}C_1D_1$	$^{13}C_0D_2$	$^{13}C_2D_1$	$^{13}C_1D_2$	$^{13}C_0D_3$	$^{13}C_2D_2$	$^{13}C_1D_3$	$^{13}C_2D_3$
	Nominal mass								
	40	41	41	42	42	42	43	43	44
	Experimental relative abundance								
	9.9	9.0	26.4	2.4	29.2	10.9	4.0	6.5	1.7
	Deviation								
	±0.2	±0.4	±0.7	±0.1	±2.5	±0.3	±0.3	±0.6	±0.1
	Theoretical relative abundances for "$C_3H_3^+$," loss of "$C_3H_3\cdot$"								
1	6.5	17.2	15.9	10.4	18.4	31.6	0	0	0
2	4.1	11.1	27.0	6.3	32.8	18.7	0	0	0
3	11.5	7.7	31.7	2.4	21.2	10.3	6.4	6.6	2.1
4	10.2	9.6	30.0	1.4	25.9	9.6	3.8	8.5	0.9

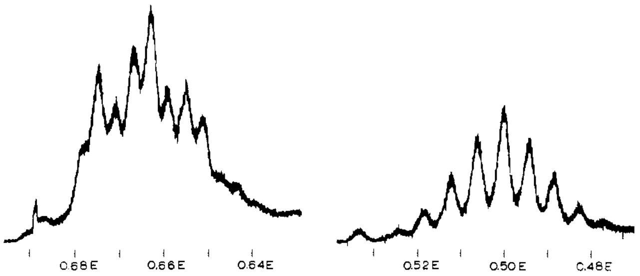


Figure 1. Partial ike spectrum of benzene-*1,2*-$^{13}C_2$-3,4,5,6-d_4 in region of loss of "$C_3H_3\cdot$" (~0.50*E*) and "C_2H_2" (~0.66*E*).

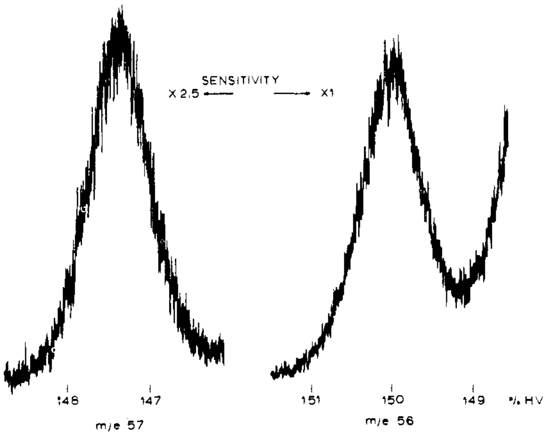


Figure 2. HV scans of benzene-*1,2*-$^{13}C_2$-*3,4,5,6*-d_4 for the transitions $84^+ \rightarrow 56^+$ and $84^+ \rightarrow 57^+$.

skirts of other peaks in some cases, their intensities can be measured accurately and are the result of only a single transition. The results of these measurements for loss of "C_2H_2" and "$C_3H_3\cdot$" from the doubly ^{13}C-labeled benzene sample are given in Table VII.

Table VII. Comparison of Theoretical and Experimental Data Derived from Metastable Ions

Case	Loss of "C_2H_2"				
	Isotopic composition of fragment ion				
	$^{13}C_0D_2$	$^{13}C_0D_3$ $^{13}C_1D_2$	$^{13}C_0D_4$ $^{13}C_1D_3$ $^{13}C_2D_2$	$^{13}C_2D_3$ $^{13}C_1D_4$	$^{13}C_2D_4$
	Nominal mass				
	54	55	56	57	58
	Exptl rel abundance				
	2.1	22.2	46.1	26.7	2.9
	Deviation				
	±0.3	±1.5	±1.6	±0.5	±0.3
	Theoretical relative abundance for "$C_4H_4\cdot^+$," loss of C_2H_2				
1	0	0	100.0	0	0
2	0	0	100.0	0	0
3	6.6	22.3	39.1	28.9	3.1
4	2.7	25.0	44.6	25.0	2.7

Case	Loss of "C_3H_3"				
	Isotopic composition of fragment ion				
	$^{13}C_0D_1$	$^{13}C_0D_2$ $^{13}C_1D_1$	$^{13}C_2D_1$ $^{13}C_1D_2$ $^{13}C_0D_3$	$^{13}C_2D_2$ $^{13}C_1D_3$	$^{13}C_2D_3$
	Nominal mass				
	40	41	42	43	44
	Exptl rel abundance				
	3.4	21.8	47.6	25.2	2.0
	Deviation				
	±0.5	±1.6	±2.0	±1.0	±0.5
	Theoretical relative abundance for "$C_3H_3^+$," loss of "$C_3H_3\cdot$"				
1	0	0	100.0	0	0
2	0	0	100.0	0	0
3	6.7	26.7	33.3	26.7	6.7
4	3.0	25.4	43.1	25.4	3.0

Discussion

Let us first consider the mass spectral data as shown in Table VI. The experimental results for loss of "C_2H_2" and "$C_3H_3\cdot$" to give ions of composition "$C_4H_4\cdot^+$" and "$C_3H_3^+$," respectively, are given together with the theoretical results for cases 1, 2, 3, and 4 calculated with the known isotopic composition of the sample (given in Table I). The uncertainty in the experimental values is approximately ±5%, except for ions of low abundance for which the error is larger, and is primarily the result of irreproducibility of intensity measurements under high-resolution conditions. Within this uncertainty, several conclusions may be drawn for this portion of the data. First, cases 1 and 2 can clearly be ruled out as participating to any significant degree. This is most clearly seen for loss of "C_2H_2" in the abundances of *m/e* 56 and 57, and for loss of "$C_3H_3\cdot$" of *m/e* 42 and 43. The extent of participation of cases 3 and 4 is not as easily distinguished. However, the data do indicate that case 4 plays the major role in the scrambling process. Case 3 may occur to a significant extent, but does not dominate. For several ions of interest, calculated ion abundances for various percentage contributions of cases 3 and 4 could easily be considered to fall within the deviations from the mean results in the experimental data.

The major difficulty in this interpretation involves the very close statistical results calculated between corresponding masses for cases 3 and 4. This is a consequence of the relatively large number of isotopically labeled molecular ion species. The differences between the statistical ion abundances for complete contribution of case 3 and that for case 4 are rather large when calculated for pure benzene-*1,2-*$^{13}C_2$*-3,4,5,6-*d_4. However, the isotopic composition of the actual sample, which is a complicated mixture of isotopically labeled benzenes, has the effect of decreasing this difference to a point where, combined with experimental uncertainty, cases 3 and 4 are difficult to differentiate.

Fortunately, such uncertainties are much less important when dealing with the metastable ion data. The experimental data are given together with the theoretically calculated results in Table VII. In this case, we can selectively look at the decomposition of the completely labeled compound, benzene-*1,2-*$^{13}C_2$*-3,4,5,6-*d_4, because although two ions may decompose to give the same daughter ion (as in the case of mass spectra), they will appear at different per cent energies on the HV scan spectra. Since their mass and energy are known, the original ion can be specified with certainty. Thus, after examination of Table VII, we can say that the predominant, if not complete, contribution of the several possible scrambling processes operating in the case of metastable ions is that of case 4. This is most clearly seen in the results from loss of "$C_3H_3\cdot$." This is a further illustration of the extreme selectivity possible when processes arising from metastable ions are studied. It becomes possible to study the origin of the various fragment ion species separately. In the normal mass spectrum, although the individual fragment ion species can be enumerated, no information is possible concerning their origin, nor indeed whether they have been formed as the result of a single or multiple stage fragmentation process.

Thus, the results from the mass spectra are subject to rather more uncertainty than those from the HV scans. Qualitatively, however, the results from the mass spectra suggest that when ions having lifetimes of approximately 10^{-7} sec are sampled, total randomization is not complete—some of the hydrogens have scrambled without scrambling of the carbon skeleton. However, the HV scans show that when ions having much greater lifetimes are sampled, *i.e.*, approximately 10^{-5} sec, complete scrambling of all atoms is seen. These results are in excellent agreement with independent work[2] in which the isotopic distributions derived from metastable peak intensities indicate complete randomization of carbons and hydrogens for loss of "C_2H_2" in benzene-*1,3,5-*$^{13}C_3$.

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