40 (C₁)   41 (Cₛ)

C_s symmetry to CH_3SiH^{2+} (42). The latter (42) is the lowest

42 (C₃ᵥ)   43 (C₄ᵥ)

44 (C₂ᵥ)

energy structure which we have found, lying 443 kJ mol⁻¹ below
10. It is characterized by a quite short C–Si bond (1.787 Å).
Another low-lying isomer is $SiCH_4^{2+}$ (43) (430 kJ mol⁻¹ below

10), while the silaethylene dication (44) lies somewhat higher in
energy (but still 348 kJ mol⁻¹ below 10). A detailed study of the
$CSiH_4^{2+}$ surface will be presented elsewhere.[38]

Concluding Remarks

Several important points emerge from this study.

(1) The HCX^{2+} dications are characterized in general by remarkably short C–X bond lengths. In the case of HCF^{2+} and $HCCl^{2+}$, the C–X bonds are the shortest yet reported for these types of bonds in gas-phase molecules.

(2) The shortening of the C–X bonds may be attributed to conjugative or hyperconjugative electron donation from X into the *pair* of formally vacant orbitals at X.

(3) Conversely, the HCX^{2+} system provides a sensitive probe of the conjugative or hyperconjugative electron-donating ability of X.

(4) With the exception of $HCCH_3^{2+}$, $HCPH_2^{2+}$, and $HCSiH_3^{2+}$, which show little or no barrier to rearrangement to more stable isomers, the remaining HCX^{2+} isomers are predicted to be experimentally observable.

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Reactions of Isolated Bicyclic Hydrocarbon Ions Excited by Different Methods

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Abstract: The molecular ions of the isomeric hydrocarbons 2-methylbicyclo[2.2.1]hept-2-ene and 2-methylenebicyclo[2.2.1]heptane retain their structural identities at low internal energies, while fragmentation of the isomers proceeds through intermediates of identical structure (e.g., ionized methylcyclopentadiene) at higher energies. Reaction intermediate scans were used to identify fragmentation intermediates not evident in other types of MS/MS data. Structures were assigned to the major odd-electron fragments on the basis of energy-resolved mass spectrometry. Activation methods which deposit a *broad range* of internal energies (electron ionization and high-energy collisional activation with a gas-phase target) or *low average* internal energies (collisional activation, surface-induced dissociation at low translational energies) produce distinct dissociation product distributions. In contrast, methods which selectively deposit high internal energies (>50 eV collisions with a surface) or which deposit relatively high energies in several steps (multiple collisions with a gaseous target at 30 eV laboratory collision energy) fail to differentiate the isomers. It is concluded that the way in which ions are energized can be a crucial factor in successful isomer distinction by mass spectrometry. Moreover, activation methods which deposit a narrow distribution of internal energies, and which are therefore desirable in isomer differentiation, should be applied over a wide range of energies if information is not to be lost.

Characterization of the numerous methods of activating ions in tandem mass spectrometry[1,2] is important for analytical applications as well as for investigations into the fundamentals of ionic processes.[3] Fragmentation of the excited ions usually takes place from a vibrationally excited ground state and may be described within the framework of the quasi-equilibrium theory.[1–3] The relative abundances of the product ions obtained by using

different methods are thus expected[1–3] to differ mainly because of differences in the internal energy distributions, P(E), of the fragmenting ions. Recently, various qualitative and semiquan-

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titative data have appeared[4,5] concerning the energy distributions of ions activated by different means. The relevance of this information in the understanding of gas-phase chemistry of complex organic ions is addressed here.

Determination of the structures of gaseous hydrocarbon ions has challenged scientists for a number of years.[3,6] The dissociation products of these ions are often the result of complex combinations of competing isomerization and dissociation reactions, which makes it difficult to distinguish between isomeric hydrocarbon ions by conventional mass spectrometric methods in some cases and to assign ion structures in others. The present study was prompted by the finding[7] that the electron ionization mass spectra of two isomeric hydrocarbons, **1** and **2**, are strikingly *different*, in spite

1   **2**   **3**
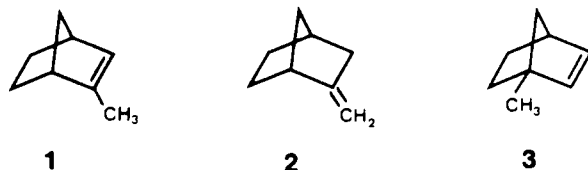
of the structural similarity between the two and the well-known[3,8] inability of the electron ionization technique to differentiate between many isomers. For example, the electron ionization mass spectra of **1** and **3** are practically identical.[7]

In this paper, attempts are made to characterize the dissociation reactions of the molecular ions of **1** and **2** by tandem mass spectrometry by using various scan modes, including the recently described reaction intermediate scan.[9] Further, the consequences of activating the ions by methods which deposit differing amounts of energy were examined. The behavior of ionized **1** and **2** was found to be strongly dependent on the way in which they are energized and can be rationalized on the basis of present knowledge concerning $P(E)$ associated with each of the activation methods. Most notably, it was discovered that in order to differentiate these isomers, it is *advantageous* to use an activation method which deposits a wide range of internal energies rather than by using more selective techniques.

Experimental Section

Low-energy collision-activated dissociation (CAD) experiments were carried out with a Finnigan triple quadrupole mass spectrometer.[10] When measuring fragment ions arising from a given parent, the instrument is set to perform daughter scans, i.e., the first quadrupole is fixed at the mass value of the parent ion of interest, and the third quadrupole is scanned for the fragments. To examine parent ions giving a specified fragment, the first quadrupole is scanned, and the third is set to pass only the chosen fragment (parent scan mode). Molecular ions were generated by 70-eV electron impact. Argon was used as the collision gas at pressures of ca. 2 mtorr for multiple-collision experiments and less than 0.1 mtorr for single-collision experiments. The potential difference between

the ion source and the rf-only quadrupole determines the axial kinetic energy or collision energy of the parent ions. In the energy-resolved experiments (ERMS[1]), successive daughter spectra were recorded as the collision energy was increased in ca. 5-eV intervals from about 5 up to 30 eV (laboratory frame). Approximate breakdown graphs were then constructed based on peak intensities normalized to the total fragment ion current at each collision energy.

The modified hybrid BQ instrument used for surface-induced dissociation (SID) experiments and the method used to acquire SID daughter spectra have been described earlier.[2c] Ions were generated by 70-eV electron impact in a source held at a potential in the range of 25–100 V with respect to ground. The ion beam was accelerated to 6 keV prior to mass analysis by the magnetic sector and decelerated prior to collision with a stainless steel surface. A picoammeter was connected to the surface, and the current due to the primary ion beam was recorded continuously during experiments. Lenses used for extraction of the emerging beam and its subsequent transfer into the quadrupole mass filter were adjusted to maximize the total ion current reaching the detector without significantly reducing the surface current. All data were taken at an incident angle of 25° (estimated uncertainty 3°) with respect to the surface normal. The angle of deviation was 120° from the original beam direction. The pressure in the chamber containing the target surface was maintained at 5.0×10^{-7} torr by means of diffusion pumps. Data acquisition was carried out by using a customized system.[11] In order to ensure identical experimental conditions, spectra of all ions with the same mass value but derived from different compounds were recorded one after another without adjustment of any instrumental parameters.

The reaction intermediate scan has been described in detail[9] and will be briefly summarized here. The experiment was performed on a prototype BEQQ hybrid mass spectrometer.[12] This instrument consists of a Finnigan MAT 212 high resolution mass spectrometer of reversed geometry, rf-only collision quadrupole and a mass analysis quadrupole. Ions were generated by 70-eV electron impact in a source held at 3 kV above ground. Argon collision gas was admitted into the first field-free region of the instrument so that multiple collisions occurred between argon and the ions generated in the ion source. The fragments generated from selected parent ions in these high-energy collisions were transmitted through the instrument by a B/E linked scan. Following deceleration by the lens assembly, these fragments were allowed to collide with argon in the rf-only quadrupole under multiple-collision conditions. The mass analysis quadrupole was set to transmit ions with a selected m/z ratio. Thus, the only ions which produce a signal are those which were formed by high-energy collisions in the first collision region *and* which fragment further in the second collision region (the rf-only quadrupole) to give the selected granddaugher ion. All bias voltages on the deceleration lens assembly and the quadrupoles were scanned during the experiment to maintain a uniform collision energy of 30 eV in the rf-only quadrupole and an optimum kinetic energy of approximately 12 eV in the mass analysis quadrupole.

Synthesis of compounds **1** and **2** is described elsewhere.[7] Ionized **4** was generated in situ in the ion source by a McLafferty rearrangement of ionized 3-(ethyl-d_5)norcamphor. 3-(Ethyl-d_5)norcamphor was prepared according to literature methods.[13] Cyclopentadiene was generated from cyclopentadiene dimer in the ion source.[14] Methylcyclopentadiene was a mixture of isomers formed in the ion source from commercial methylcyclopentadiene dimer. Cyclohexa-1,3-diene and bicyclo[2.2.1]-heptan-2-one (**5**) were obtained commercially.

Results

Dissociation Caused by Different Activation Methods. Upon 70-eV electron ionization (EI), 2-methylbicyclo[2.2.1]hept-2-ene (**1**) yields the ion of m/z 80 due to loss of C_2H_4 as the major fragment ion.[7] Excluding the ion of m/z 79 (35%), all other fragment ions have a relative abundance of less than 12%. In a notable contrast, 2-methylenebicyclo[2.2.1]heptane (**2**) gives several abundant fragment ions, the major ones arising by loss of C_2H_5 (m/z 79, 100%), C_3H_6 (m/z 66, 82%), and CH_3 (m/z 93, 69%). The spectra obtained[7] by high-energy (3-keV) collisions of molecular ions of **1** and **2** with He target show the same major

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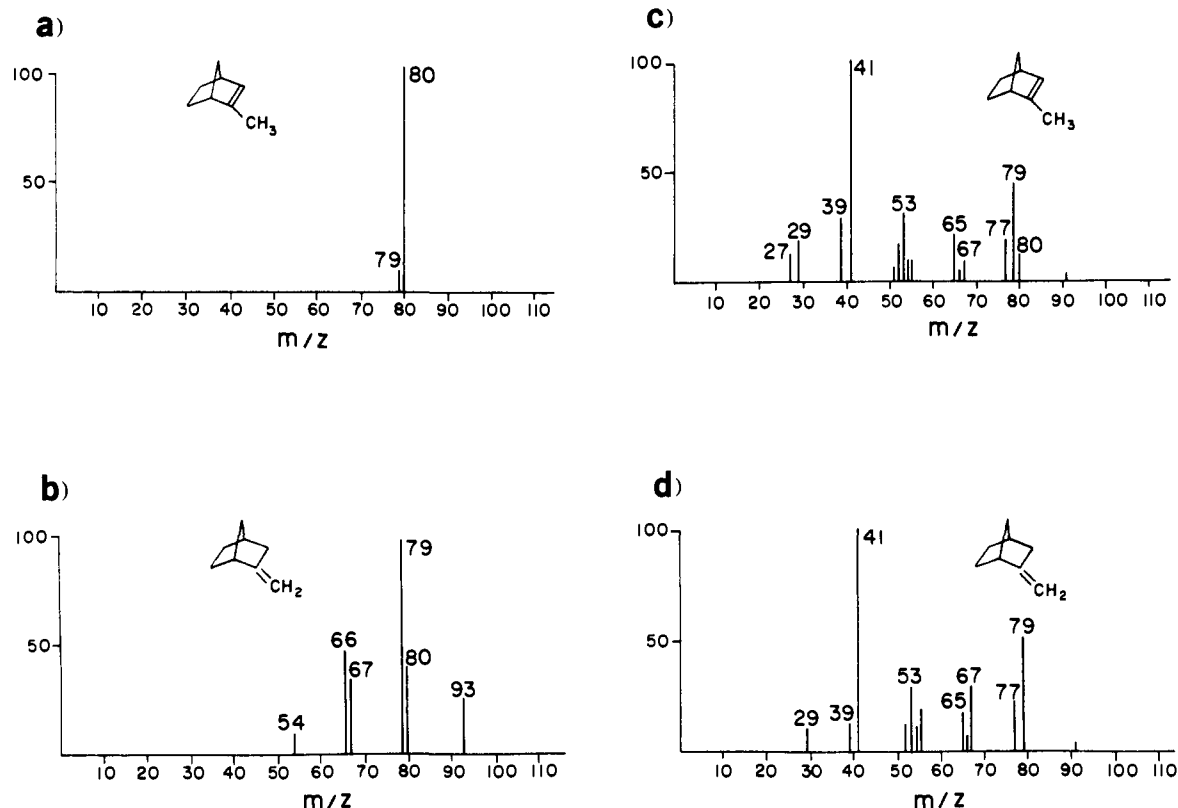
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Figure 1. Surface-induced dissociation daughter spectra of the molecular ions of (a) **1** and (b) **2** at low kinetic energy (25 eV) and (c) and (d) at higher kinetic energies (51 and 63 eV, respectively).

products as the corresponding electron ionization mass spectra (ions with a relative abundance of at least 6% are *m/z* 39 (6%), 77 (6), 79 (9), 80 (49) for **1** and *m/z* 39 (8), 66 (23), 77 (7), 79 (15), 93 (6) for **2**.

Surface-induced dissociation[2c,15] (SID) of ionized **1** and **2** at 25-eV collision energy yields product distributions (Figure 1 (parts a and b)) which are distinctly different from each other and which bear some resemblance to the EI mass spectra and to the high-energy collision-activated dissociation (CAD) daughter spectra obtained for each of the isomers. Quite unexpectedly, the dissociation patterns obtained from the isomers become increasingly similar when the collision energy is increased (Figure 1 (parts c and d)). This behavior is even more apparent when surface-induced dissociation is preformed over a range of collision energies and the data are plotted as breakdown curves (Figure 2). The strikingly different behavior at low energy is replaced by a common set of fragment ions with similar relative abundances at higher energy. It is also seen that ionized **2** requires less energy than **1** to produce the fragment ions common to the isomers. Interestingly, the large abundances of low-mass ions (e.g., *m/z* 41) at collision energies of 50 eV and above indicate that a larger average energy can be deposited in ions by collisions with a surface than upon 70-eV electron ionization of the corresponding neutrals. Similar results have been reported from other systems.[5b,15]

Low-energy (28 eV) CAD daughter spectra obtained by using single-collision conditions for ionized **1** and **2** (Figure 3 (parts a and b)) are markedly different from each other and similar to those obtained by low-energy SID for each of the isomers. When target pressure was increased so that multiple activating collisions occurred, the product distributions of the isomers became similar (Figures 3 (parts c and d)). Spectra measured as a function of ion kinetic energy (energy-resolved mass spectra,[1] ERMS) are presented in the form of breakdown graphs (Figure 4) which show that the differences in the fragmentation patterns are substantial

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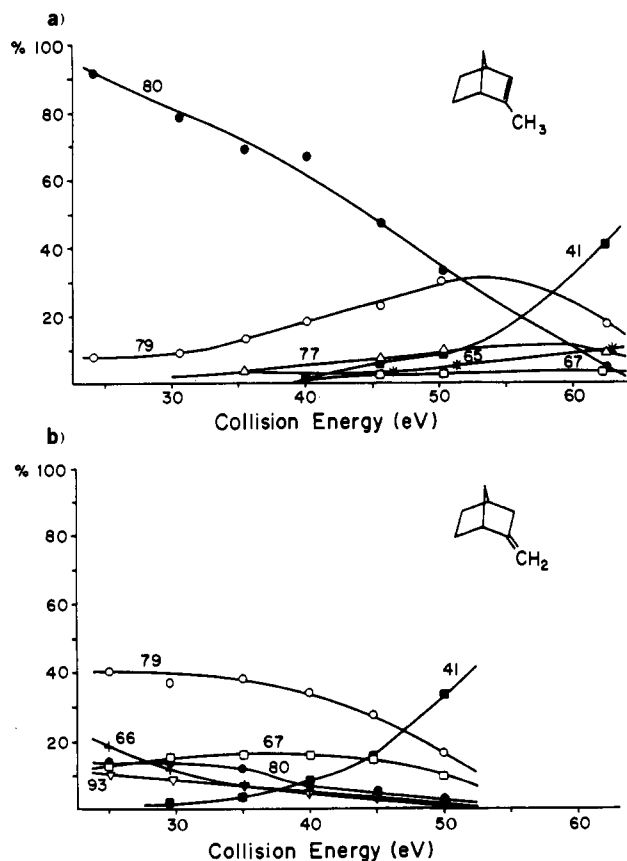

Figure 2. Breakdown curves obtained by surface-induced dissociation for the molecular ions of (a) **1** and (b) **2**.

at low-collision energies but diminish as higher collision energies are approached. These observations are consistent with those made for surface-induced dissociation. Two additional conclusions can

Table I. Parent Spectra of Fragment Ions from **1** and **2**, 28-eV, Single-Collision Conditions[a]

daughter ion (m/z)	parent ions m/z (%)	
	1	**2**
93	94 (13), 108 (100)	94 (14), 108 (100)
91	92 (40), 93 (100), 107 (24), 108 (16)	92 (8), 93 (100), 107 (11)
80	81 (12), 108 (100)	81 (24), 108 (100), 109 (23)
79	80 (100)	80 (100), 107 (9), 108 (83)
77	79 (100), 80 (23), 93 (16), 108 (7)	78 (9), 79 (100), 93 (90), 108 (8)
66	67 (39), 81 (100), 92 (41), 108 (32)	67 (16), 108 (100)
51	52 (12), 77 (100), 79 (35), 91 (7)	52 (18), 66 (10), 77 (100), 79 (50), 91 (8), 93 (12)
41	67 (15), 80 (100), 81 (17), 91 (9), 93 (6), 95 (24)	67 (100), 80 (32), 81 (6), 91 (17), 93 (64), 108 (8)
39	40 (23), 54 (7), 65 (49), 79 (52), 80 (100), 91 (20)	40 (36), 41 (49), 54 (53), 65 (95), 66 (100), 67 (50), 78 (15), 79 (99), 80 (34), 91 (26), 93 (17)

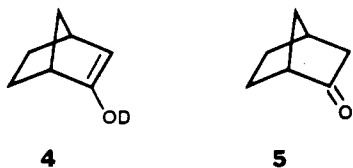[a] Peaks with a relative intensity of more than 6% are reported.

Table II. Parent Spectra of Fragment Ions from **1** and **2**, 28-eV, Multiple-Collision Conditions[a]

daughter ion (m/z)	parent ions m/z (%)	
	1	**2**
93	95 (7), 108 (100)	108 (100), 109 (10)
91	92 (28), 93 (66), 106 (17), 107 (25), 108 (100), 109 (6)	92 (5), 93 (94), 107 (16), 108 (100), 109 (5)
80	81 (17), 108 (100), 109 (23)	81 (30), 108 (100), 109 (98)
79	80 (68), 108 (100)	80 (18), 108 (100)
77	79 (30), 80 (100), 93 (4), 108 (39)	79 (59), 80 (17), 93 (36), 108 (100)
66	67 (11), 81 (74), 92 (35), 94 (11), 96 (16), 108 (29), 109 (55)	108 (100)
65	66 (17), 80 (100), 91 (64), 93 (18), 95 (15), 96 (7), 107 (7), 108 (51), 109 (5)	66 (78), 80 (12), 91 (76), 93 (71), 107 (15), 108 (100)
51	77 (24), 79 (98), 80 (100), 93 (14), 108 (6)	66 (5), 77 (28), 79 (100), 80 (11), 93 (64), 108 (15)
39	65 (5), 66 (8), 79 (7), 80 (100), 91 (13), 95 (6)	41 (6), 54 (6), 65 (14), 66 (100), 67 (26), 79 (26), 80 (20), 91 (27), 93 (24), 108 (12)

[a] Peaks with a relative intensity of more than 4% are reported.

Table III. Daughter Spectra of Fragment Ions from **1** and **2**, 28-eV, Single-Collision Conditions[a]

parent ion (m/z)	fragment ions m/z (%)	
	1	**2**
93	78 (18), 77 (100), 76 (6), 65 (8), 53 (12), 52 (11), 41 (53)	78 (11), 77 (100), 65 (9), 53 (9), 51 (5), 41 (14)
91	65 (100), 64 (6), 63 (15), 51 (15), 41 (24), 39 (23)	65 (100), 63 (6), 51 (7), 41 (16), 39 (13)
80	65 (88), 54 (12), 53 (28), 52 (81), 51 (12), 41 (100), 40 (10), 39 (66), 28 (5), 27 (7)	65 (80), 54 (27), 53 (29), 52 (100), 51 (20), 41 (65), 40 (7), 39 (46), 28 (5), 27 (5)
79	53 (91), 51 (100), 39 (65), 29 (6), 27 (52)	53 (100), 51 (56), 39 (33), 27 (17)
77	51 (100), 50 (6), 27 (16)	51 (100), 50 (7), 27 (10)
66	53 (7), 51 (27), 40 (100), 39 (70), 38 (9), 27 (40)	51 (13), 40 (100), 39 (49), 38 (6), 27 (11)
65	39 (100), 38 (9)	39 (100), 38 (5)

[a] Peaks with a relative intensity of more than 5% are reported. The mass range within a few mass units of the parent ion was not examined.

Table IV. Daughter Spectra of Fragment Ions from **1** and **2**, 28-eV, Multiple-Collision Conditions[a]

parent ion (m/z)	fragment ions m/z (%)	
	1	**2**
107	91 (61), 79 (7), 78 (6), 77 (46), 65 (100), 63 (9), 53 (6), 51 (30), 41 (16), 39 (30), 27 (6)	91 (70), 79 (19), 77 (68), 65 n100), 63 (11), 53 (5), 51 (29), 50 (7), 41 (24), 39 (39), 29 (5)
93	91 (6), 78 (5), 77 (29), 65 (11), 51 (100), 50 (19), 41 (7), 39 (15)	91 (11), 78 (6), 77 (45), 65 (14), 51 (100), 50 (20), 41 (7), 39 (17)
91	65 (47), 63 (15), 62 (9), 51 (15), 50 (9), 41 (11), 39 (100)	65 (76), 63 (18), 62 (11), 51 (15), 50 (10), 41 (10), 39 (100)
80	79 (38), 77 (100), 65 (8), 53 (8), 52 (16), 51 (87), 50 (22), 41 (12), 39 (87), 27 (4), 26 (6)	79 (38), 78 (12), 77 (100), 65 (6), 53 (8), 52 (30), 51 (96), 50 (24), 41 (7), 39 (58), 27 (4)
79	77 (35), 51 (100), 50 (24), 39 (8), 27 (10)	77 (50), 53 (7), 51 (100), 50 (35), 39 (10), 27 (8)
77	74 (5), 51 (100), 50 (80), 27 (6)	74 (6), 51 (100), 50 (90), 27 (4)
67	51 (5), 50 (5), 41 (42), 40 (8), 39 (100), 38 (8), 37 (5), 27 (6)	51 (4), 50 (7), 41 (41), 40 (13), 39 (100), 38 (12), 37 (6), 27 (9), 26 (5)
66	65 (15), 51 (14), 50 (13), 40 (24), 39 (100), 38 (13), 37 (5), 27 (7)	65 (27), 51 (18), 50 (15), 40 (26), 39 (100), 27 (4)
65	63 (10), 62 (7), 39 (100), 38 (29), 37 (14)	63 (8), 62 (7), 39 (100), 38 (18), 37 (12)

[a] Peaks with a relative intensity of more than 4% are reported.

be drawn by comparing the SID and CAD breakdown graphs (Figures 2 and 4). First, collisional activation does not deposit the internal energies necessary to achieve similar fragment ion abundances as seen for the two isomers in SID, although the results tend toward this as the collision energy is raised. Second, in CAD as well as in SID, more energy has to be deposited in ionized **1** than **2** in order to obtain similar fragmentation patterns for the isomers.

In contrast with the behavior of the molecular ions of the hydrocarbon isomers **1** and **2**, the analogous oxygen-containing ions, ionized **4** and **5**, yield different CAD product distributions

loses C_2H_4 whereas ionized **5** gives a dominant product ion of m/z 66 by loss of C_2H_4O. These reactions are analogous to those which dominate for **1** and **2** at low excitation energies, i.e., **1** loses C_2H_4 whereas **2** gives 66^+.

Fragmentation Pathways. Parent and daughter scan modes[1] as well as the recently developed reaction intermediate scan[9] were used to examine the dissociation processes which occur for **1** and **2**. Parent spectra, obtained for a large number of selected fragment ions by using both single- and multiple-collision conditions, are presented in Tables I and II, respectively. These spectra identify the precursors to the selected ions. Note that the relative intensities of the peaks in these spectra are not only dependent on the extent to which each parent ion fragments to the given daughter ion but also on the differing ratios in which the precursor ions are formed in the ion source. Complementary information acquired by recording daughter spectra for several ions under single- or multiple-collision conditions is presented in Tables III and IV, respectively. Additional daughter spectra were
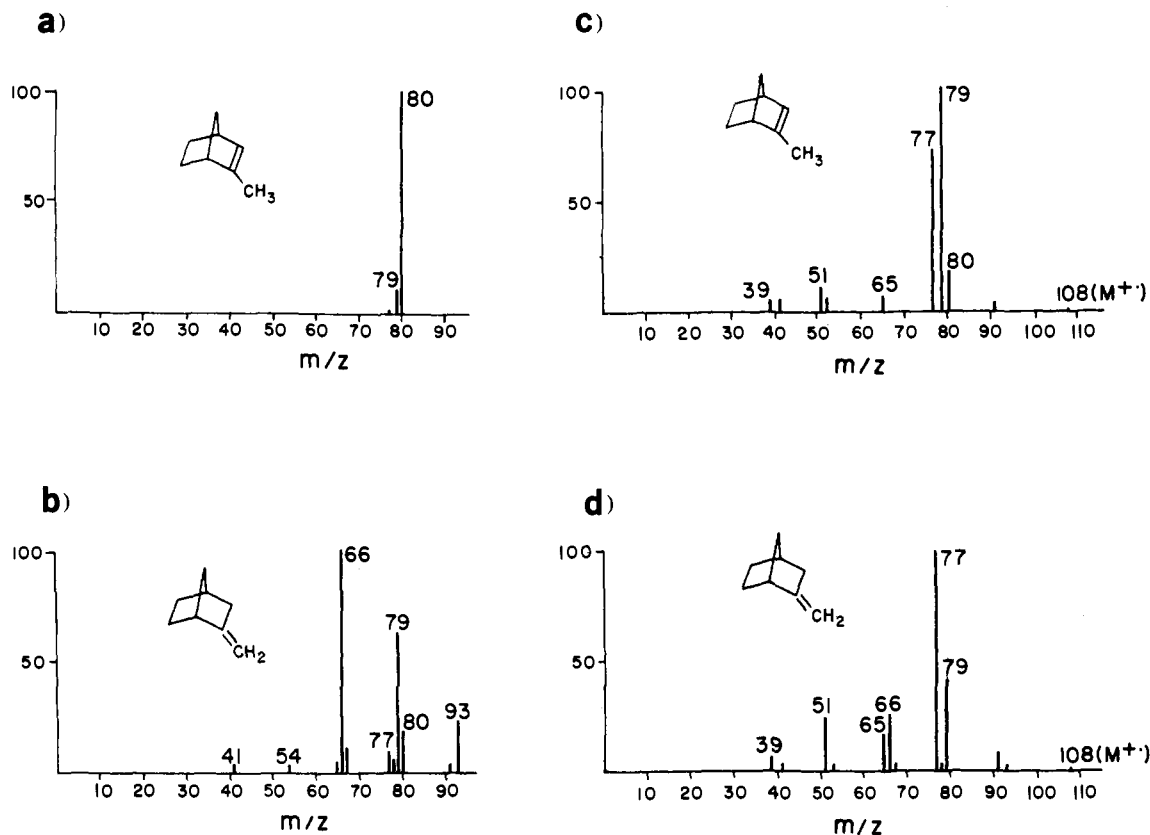
under all experimental conditions used. Ionized **4** preferentially

4   **5**

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Figure 3. Collision-activated dissociation daughter spectra obtained for the molecular ions of (a) **1** and (b) **2** under single-collision conditions and (c) and (d) under multiple-collision conditions at low (28-eV) collision energy.

obtained for the fragment ions of m/z 79 and 80 by employing surface-induced dissociation (Figure 5). Reaction intermediate scans were employed to determine the intermediate species connecting the molecular ions of **1** and **2** and the fragment ions of m/z 41 (Figure 6) and m/z 79 (only two peaks, at m/z 80 and m/z 107, are present in these spectra). This large set of data shows that fragment ions with the same mass value but derived from different isomers fragment by similar dissociation pathways. This applies to all collision energies used in CAD and SID, as well as to both single- and multiple-collision conditions in CAD.

Common intermediate species were found to occur en route from the isomeric molecular ions to the fragment ions of m/z 41 and 79. However, the reaction intermediate spectra show substantially different intensities for the signals of the intermediates. These differences reflect the characteristic behavior of ionized **1** and **2**. For example, only in the case of **1** does the intermediate 80^+ make a large contribution to formation of 41^+. This signifies favored formation of 80^+ upon fragmentation of ionized **1** but not **2**. Note that the most intense signals in the reaction intermediate spectra were obtained for intermediates of m/z 107 (Figure 6). This discovery was quite unexpected since ions of m/z 107 are minor components or absent in the product distributions obtained from **1** and **2** upon EI, CAD, or SID. The parent spectra of 91^+ (Tables I and II) and the daughter spectra of 107^+ (Table IV) confirm that 107^+ occurs en route from **1** and **2** to 91^+ and further to 41^+. Detailed consideration of all the data presented shows that major pathways leading to the most abundant fragment ions of ionized **1** and **2** are those shown below (Scheme I).

Ion Structures. The similarity found in the dissociation product distributions of most fragment ions with the same mass-to-charge value (but derived from different isomers) suggests similar structures for these fragment ions. The major odd-electron ions (m/z 66 and m/z 80) are of special interest. The ion of m/z 66, which is formed in dramatically different amounts for the two isomers, seems nevertheless to have a mixture of structures[16] which is independent of the source from which it is generated (see Tables
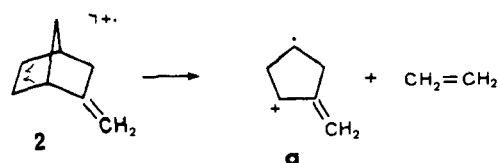
(16) Mabud, Md. A.; Ast, T.; Cooks, R. G. *Org. Mass Spectrom.*, in press.
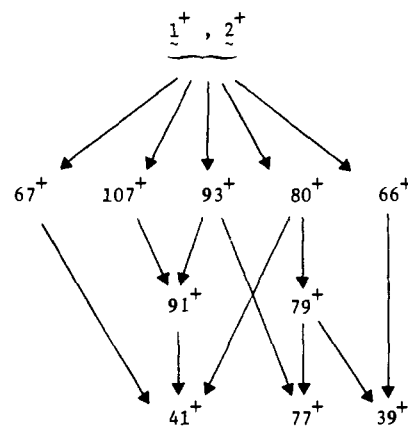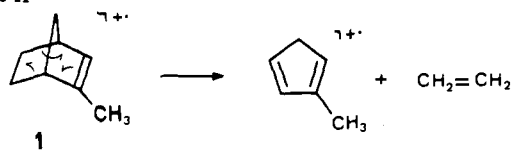
Scheme I

Scheme II

Scheme III

III and IV). The same mixture of cyclic and linear structures is generated[16] from cyclopentadiene (molecular weight 66) upon electron ionization (multiple-collision, 28-eV CAD spectrum of the molecular ion of cyclopentadiene: m/z 65 (13%), 51 (11), 50 (11), 40 (17), 39 (100), 38 (7), 27 (6)) and from **5**.
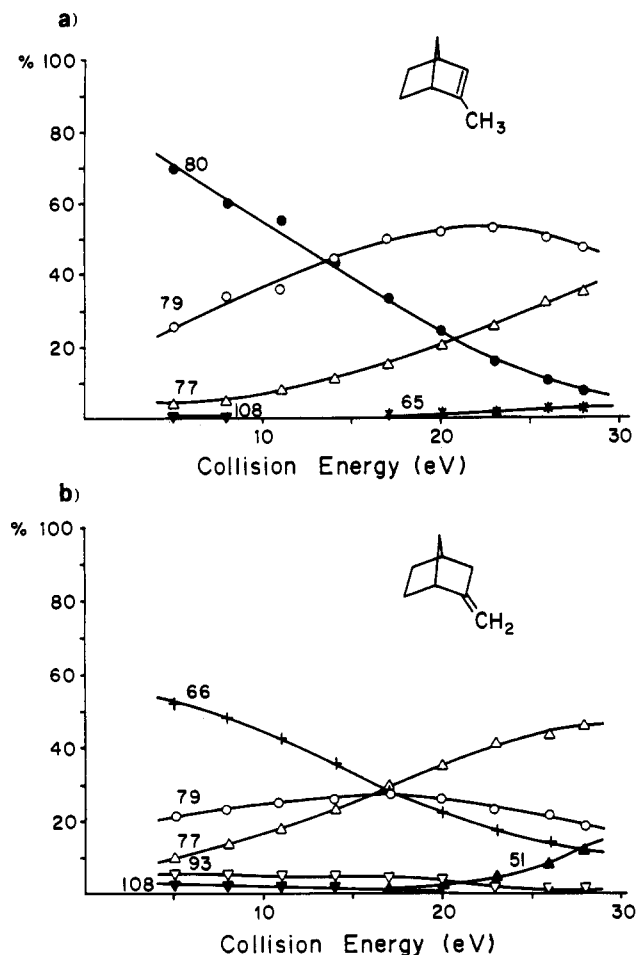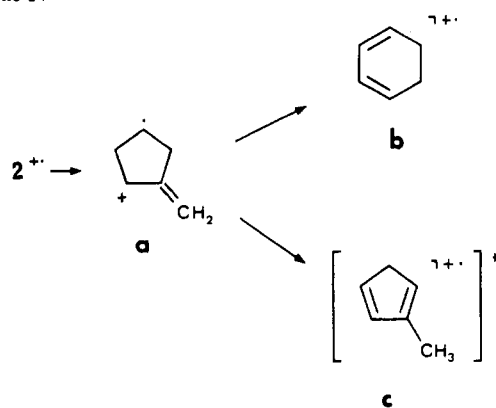
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a)

b)

Figure 4. Breakdown curves obtained by low-energy CAD for the molecular ions of (a) 1 and (b) 2 under multiple-collision conditions.

The fragment ion of m/z 80 is presumably[7,17] formed by a retro-Diels–Alder reaction from the isomer 1 (Scheme II). Simple ethylene elimination from ionized 2, which cannot undergo the retro-Diels–Alder reaction from an unrearranged structure, would lead at least initially to a different product (Scheme III). To examine the structure of the ions 80$^+$ derived from 1 and 2, ERMS data were recorded for these ions by employing CAD under single- as well as multiple-collision conditions and compared with ERMS data measured for ionized methylcyclopentadiene and cyclohexa-1,3-diene. Ionized methylcyclopentadiene is expected[18] to have a mixture of methylcyclopentadienyl and cyclohexadienyl structures, while ionized cyclohexa-1,3-diene has been suggested[18] to have the cyclohexadienyl structure. The main differences found in the ERMS data (Figure 7) are slightly different relative abundances of ions of m/z 78, these ions being most abundant for 2 and cyclohexadiene. Only a very small amount of 78$^+$ is formed for 1 (see also Figure 5 (parts c and d)). These results suggest that the stable ions of m/z 80 derived from 2 and cyclohexadiene have similar structures, whereas those generated from 1 probably have the methylcyclopentadienyl structure.

Discussion

Dissociation Behavior. The most significant differences in the fragmentation behavior of ionized 1 and 2 are associated with the lowest energy pathways, those which lead via elimination of stable neutral molecules to the odd-electron ions of m/z 66 and 80. The formation of the former ion requires migration of two hydrogen atoms. For isomer 2, this slow process dominates under conditions

(17) See, also: Kluft, E.; Nibbering, N. M. M.; Kuhn, H.; Herzschuh, R. *J. Am. Chem. Soc.* **1986**, *108*, 7201.
(18) Smith, T. E.; Smith, S. R.; McLafferty, F. W. *Org. Mass Spectrom.* **1978**, *13*, 254.

Scheme IV

where the parent ion is not highly energized. In contrast, ionized 1 predominantly fragments to the other odd-electron ion (m/z 80) under low-energy conditions. This behavior, favored formation of m/z 80 by a retro-Diels–Alder reaction for 1 as well as for the oxygen-containing analogue 4 but not for 2 (or 5), suggests that at least at low-excitation energies, ionized 1 retains its structure. In experiments in which more energy is deposited in ionized 1 and 2, formation of 66$^+$ and 80$^+$ cannot compete with faster reactions which lead to similar product distributions for the isomers.

The similarity of the dissociation pathways of the ionized isomers as well as the identity of structures of the major fragment ions, and, on the other hand, the drastic differences in the relative abundances of 66$^+$ and 80$^+$ formed from ionized 1 and 2 at low-excitation energies suggest two possibilities regarding ion structural questions: (i) The molecular ions undergo partial interconversion between two or more structures *prior to* activation or dissociation so that the fragmenting ions have a mixture of structures which are the same for the isomers but occur in different proportions. (ii) The ionized isomers *retain* their structures and fragment differently but at higher energies produce fragments with the same structure, possibly via common intermediate species. The SID daughter spectra obtained by using higher collision energies for the molecular ions of 1 and 2 and for the fragment ions 80$^+$ derived from 1 are similar, supporting the latter interpretation (see Figures 1 and 5 (parts c and d)) and the possibility that much fragmentation of 1 and 2 occurs via ionized methylcyclopentadiene (m/z 80) at higher energies. The CAD spectra obtained by using high target pressures for the molecular ions of 1 and 2 (Figure 3 (parts c and d)) also are remarkably similar to the daughter spectrum of 80$^+$ generated from 1 (major products at 2 mtorr and 16 eV: m/z 79 (100%), 78 (2), 77 (85), 65 (3), 52 (3), 51 (3)). Note that these results, considered together with those given above in conjunction with the discussion of Scheme III, suggest at least three different structures for 80$^+$ generated from 2. The *stable* ions of m/z 80 are sampled in experiments where parent and daughter spectra are recorded for 80$^+$. The results obtained from these experiments suggest the cyclohexadienyl structure for the stable ions of m/z 80. We propose that these ions (b in Scheme IV) are formed by a low-energy isomerization of initially formed less stable ions of m/z 80 which may have the structure indicated in Schemes III and IV (structure a). When energized sufficiently, the transient ions a do not isomerize to b but instead undergo fast hydrogen shifts to generate excited methylcyclopentadienyl ions c which rapidly fragment to give product distributions characteristic for ionized methylcyclopentadiene.

The hypothesis presented above is supported by several observations: (i) ionized 2 does not yield abundant ions 80$^+$; (ii) the stable ions of m/z 80 which are formed from 2 have the cyclohexadienyl structure, *not* the methylcyclopentadienyl structure, in spite of the fact that ionized 2 gives fragmentation patterns characteristic for ionized methylcyclopentadiene at high-excitation energies; (iii) more energy is needed in ionized 1 than 2 to produce fragmentation patterns characteristic for ionized methylcyclopentadiene (ionized 1 with low amounts of
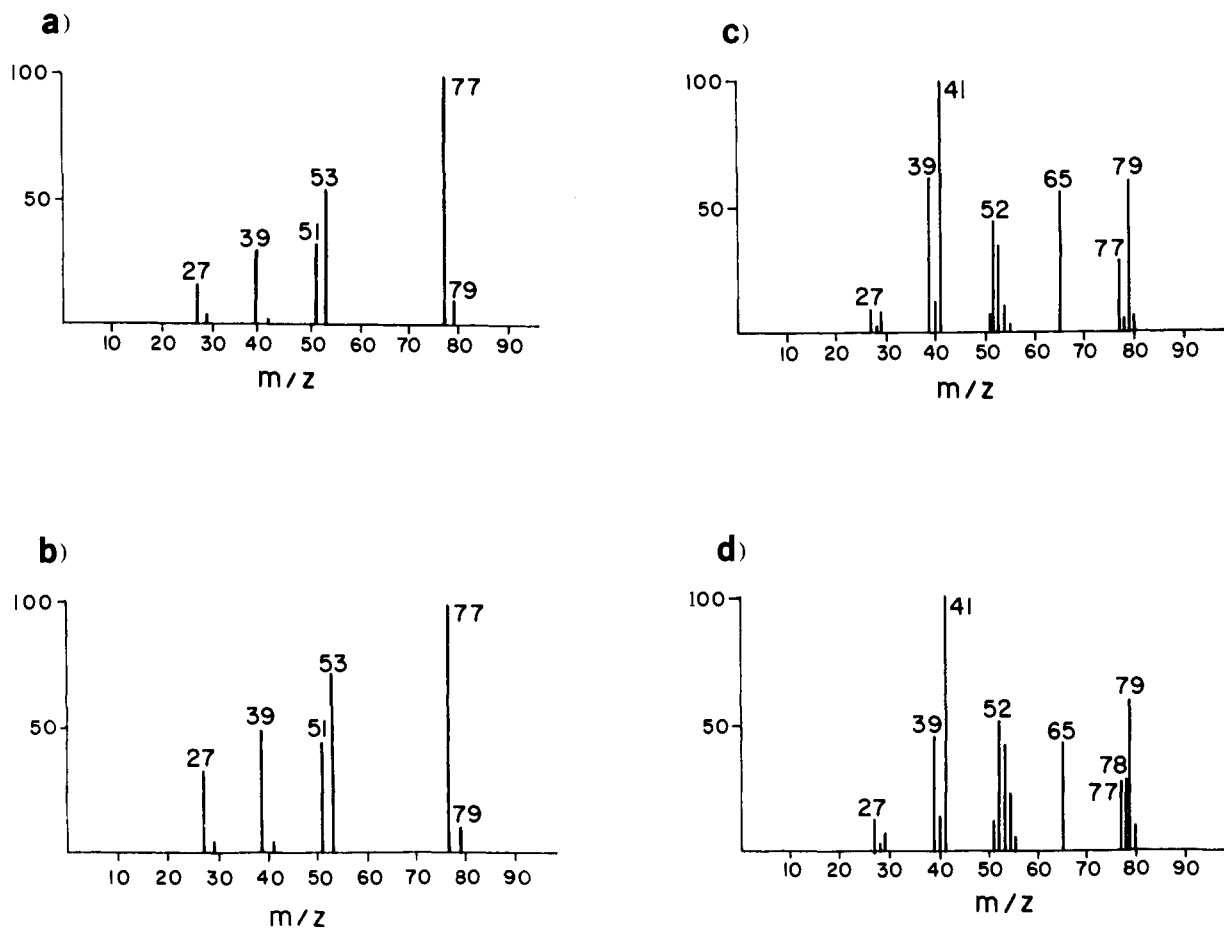
Figure 5. Surface-induced dissociation daughter spectra obtained by using 40-eV collision energy (a) and (b) for ion of m/z 79 and (c) and (d) for ion of m/z 80 derived from **1** and **2**, respectively.
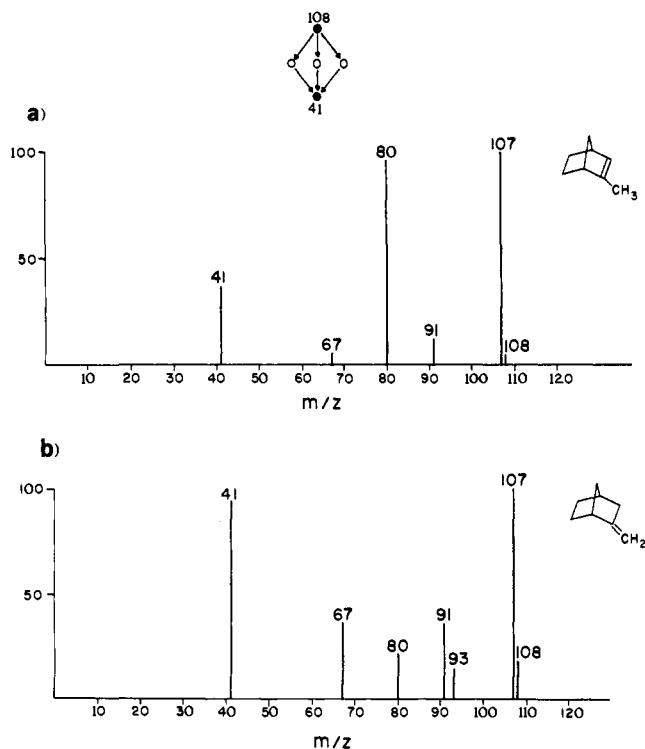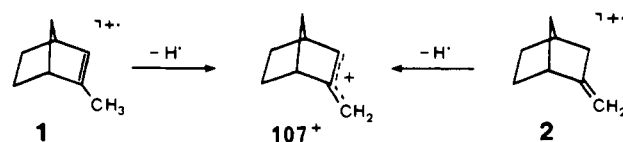

Figure 6. Reaction intermediate spectra connecting the molecular ions of **1** and **2** to ion of m/z 41: (a) isomer **1** and (b) isomer **2**.

internal energy fragments to low-energy methylcyclopentadienyl ions by a retro-Diels–Alder reaction while ionized **2** yields methylcyclopentadienyl ions with excess internal energy due to the preceding exothermic isomerization **a** → **c**).

Scheme V

The reaction intermediate spectra (Figure 6) provide further clues as to the identity of the common intermediates. They show not only the ion of m/z 80 as an obvious candidate but also reveal another important common intermediate, the ion m/z 107. This ion is formed by loss of H• from ionized **1** and **2**, presumably as shown in Scheme V.

Effects of Different Activation Methods. The gross features of the spectra obtained for **1** and **2** by using different activation methods can be explained on the basis of differing internal energy distributions, $P(E)$, deposited in the parent ions with these methods,[19] assuming that the fragmentation may be described by the quasi-equilibrium theory.[1,20] For 70-eV electron ionization as well as high-energy collisional activation, internal energy distributions are characteristically broad, extending to very high energies[4,5] which is not true for $P(E)$ deposited by low-energy collisional activation.[5] Surface-induced dissociation results in particularly narrow internal energy distributions.[5b] Consistent with this, electron ionization as well as high-energy CAD produces fragments from low-energy processes (e.g., m/z 80 and 66) along with small fragments originating from high-energy processes. In contrast, single-collision low-energy CAD only yields abundant low-energy fragment ions. The product distributions obtained by

(19) The lifetimes of the ions prior to excitation as well as their decomposition times after excitation are comparable for the activation methods used in the present study (1–10 × 10⁻⁶ s).

(20) Rosenstock, H. M.; Wallenstein, M. B.; Wahrhafting, A. L.; Eyring, H. *Proc. Natl. Acad. Sci. U.S.A.* **1952**, *38*, 667.
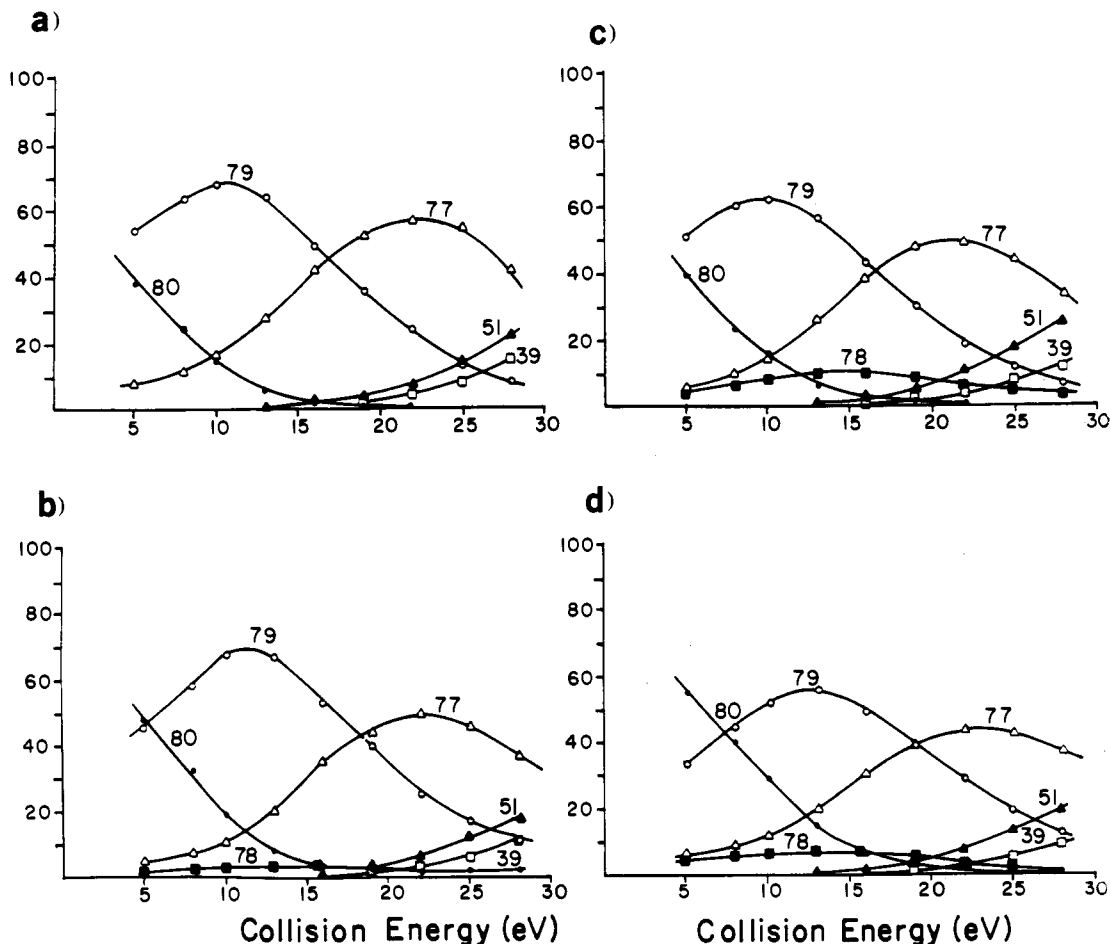
a)

c)

b)

d)

Collision Energy (eV)   **Collision Energy (eV)**

Figure 7. Breakdown curves obtained by low-energy CAD for m/z 80 generated from different precursors: (a) isomer **1**, (b) isomer **2**, (c) methyl-cyclopentadiene, and (d) cyclohexa-1,3-diene.

25-eV collisions with a surface can be rationalized by a narrow internal energy distribution of relatively low-average energy (no molecular ion, no fragment ions of low-mass values).[5b] At higher impact energies, the average energy imparted in collisions with a surface increases rapidly, and, as a result, extensive fragmentation occurs.

It was discovered that the spectra obtained by depositing *small average energies* in the parent ions are different for the two isomers whereas those obtained by depositing large average energies are not. This finding contrasts with the widely held view that maximization of energy deposition is desirable in order to differentiate closely similar ion structures since low-energy ions often favor isomerization reactions over structurally characteristic simple bond cleavages.[3,21–23] It should be noted here that activation caused by absorption of multiple infrared photons,[24] which predominantly results in dissociation by the lowest energy reaction, should be an especially useful method in differentiation of isomers behaving like ionized **1** and **2**. Isomer distinction by multiple-collision CAD has several potential problems, including the high probability of the ions being isomerized by collisions which deposit insufficient energy for dissociation to take place prior to actual CAD.[23]

Conclusions

(i) In spite of the different electron ionization mass spectra of **1** and **2**, the fragmentation pathways of the molecular ions of these compounds are very similar. Upon excitation, ionized **1** and **2**

fragment to similar products, the relative abundances of which are strongly dependent on the excitation energy. The differing product distributions obtained for these ions at low excitation energies suggest that they retain distinct structures. At higher excitation energies, fragmentation proceeds through common intermediates, ionized methylcyclopentadiene being the most prominent one. The important role of the transient ions 107^+ in fragmentation of ionized **1** and **2** was revealed by reaction intermediate spectra obtained by a new scan mode. This information is not readily available from the other experiments.

(ii) Ionized **1** and **2** produce different dissociation product distributions only when they are activated by a method which deposits a *broad* $P(E)$ (EI, high-energy collisional activation) or a $P(E)$ with a *low average energy* (high- and low-energy collisional activation, collisions with a surface at low ion kinetic energy). This discovery is important considering the current tendency (i) to favor activation methods which deposit a narrow $P(E)$ and (ii) to maximize the energy deposition in order to cause structurally diagnostic decompositions.[1,2,15,25] It is not known how often such exceptional behavior as found for **1** and **2** is likely to be encountered. It is concluded that selective activation methods should be applied over a range of internal energies if information is not to be lost.

(iii) Ion activation through collisions with a surface is an especially promising new method because it results in a relatively narrow $P(E)$ which can be readily varied over a wide range of energies.

(21) Ast, T. *Adv. Mass Spectrosc., Part A* **1986**, 471.
(22) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: New York, 1973.
(23) Kenttämaa, H. I.; Cooks, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 1881.
(24) Thorne, L. R.; Beauchamp, J. L. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3.

(25) Silberstein, J.; Levine, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 8284.