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GAS PHASE REACTIVITIES OF ISOMERIC IONS: METHYLENEDIPHENYLCYCLOPROPANE AND DIPHENYLMETHYLENECYCLOPROPANE

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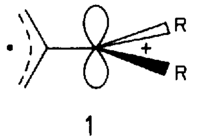
ABSTRACT

Gas phase ion/molecule reactions have been used to probe the structure of ions obtained by electron impact upon 1-(diphenylmethylene)cyclopropane and 2,2-diphenyl-1-methylenecyclopropane. The resulting ions of molecular composition $C_{16}H_{14}$ (m/z 206$^+$) were reacted with charge transfer reagents ($6{\cdot}9 < IP < 8{\cdot}8$eV), giving evidence for the presence of isomeric ions with different reactivities. The less reactive ion is identified as a trimethylenemethane species (TMM$^+$) in which one cyclopropane bond is broken; the more reactive ions are assigned as vertical ions in which the cyclopropane ring is unaffected. The vertical ions have recombination energies of $8{\cdot}44 \pm 0{\cdot}05$eV, whereas TMM$^+$ has one of $7{\cdot}41 \pm 0{\cdot}05$eV. The TMM$^+$ fraction is not constant; it increases with increasing IP of the reagent. This is attributed to a reagent-catalyzed isomerization of the vertical ion to TMM$^+$. In addition, the reagent ions are observed to undergo a unique reaction with the neutral methylenecyclopropane derivatives: electron transfer and ring opening to yield TMM$^+$. These findings limit the application of the customary equilibrium measurements as a method to determine the substrate IP.

INTRODUCTION

The thermal and photochemical rearrangements of methylenecyclopropane and its derivatives have attracted much interest because of the unusual nature of the intermediates and/or transition states through which the reorganization proceeds.[1–5] More recently, electron transfer induced isomerizations of methylenecyclopropane systems have been studied. A radical cation with a bisected trimethylenemethane structure (**1**, R = C_6H_5) was suggested as the most logical intermediate.[6] This assignment is further supported by the results of nuclear spin polarization (CIDNP) experiments.[7] The same technique also indicated the existence of a second type of methylenecyclopropane radical cation, in which the spin is, in essence, localized in the olefinic moiety, and the cyclopropane ring is unaffected (**2**, R = C_6H_5).[7]



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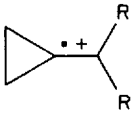

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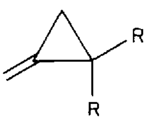
The generation and observation of these species in solution is characterized by three features: they are generated by a comparatively mild method, viz. electron transfer to a photoexcited acceptor molelcule; any excess energy is rapidly dissipated; and the lifetimes of the individual radical cations are limited, because of rapid electron return from the geminate acceptor radical anion. Accordingly, only radical ion rearrangements with relatively low barriers are observed.[8]

It was of interest to extend the investigation of these species to reaction conditions under which they can be generated with a wider range of energies, and under which the dissipation of excess energy is inefficient. These conditions are met in the gas phase; accordingly Fourier transform mass spectrometry appeared to be the best method.[9,10] It should be noted that some energy is dissipated by bond cleavage to form fragment ions typically observed in a mass spectrum. There is still energy retained in the unfragmented gas phase ions which is insufficient for causing fragmentation to a lower mass ion but still in excess of the amount of excess energy present for an ion in solution.

The trimethylenemethane ion (TMM$^+$, **1**) can be approached from two precursors, 2,2-diphenyl-1-methylenecyclopropane (*asym*-MCP, **3**) and 1-(diphenylmethylene)cyclopropane (*sym*-MCP, **4**). Our objectives in the present study were to determine whether the nonvertical ion **1** was formed in the gas phase from either *asym*-MCP or *sym*-MCP and the fraction of this species if it was not the exclusive structure present.

Two 'localized' methylenecyclopropane ions must be considered as alternatives, the more stable 'diphenylethene-type' ion, **2**, and the less stable 'diphenylcyclopropane' ion, **5**, which is the molecular ion derived from **3**. The former ion has been implicated as an intermediate in solution[7] whereas the latter, under the same conditions, could only be a fleeting intermediate, with a lifetime shorter than a nanosecond.[7]



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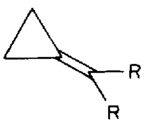

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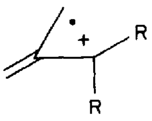

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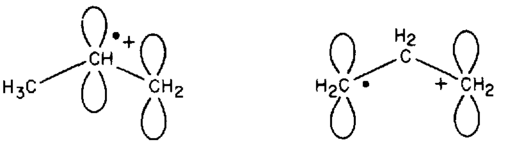
Differentiating and assigning ion structures in the gas phase is not straighforward since a structure can only be inferred from experiments in which the ions are perturbed. In this study, selective ion/molecule reactions were evaluated, a method similar to that used to differentiate the isomeric ions of m/z 42^+ generated by electron impact on cyclopropane. The reactions of these ions with NH_3 included proton transfer as well as formation of CNH_4^+ and CNH_5^+.[11,12] Convincing evidence for the existence of two isomeric ions was presented. At ionization energies just above the ionization potential (IP) of cyclopropane the extent of proton transfer to NH_3 was dependent upon ionization energy. This finding was rationalized by postulating an energy dependent ring-opening process. However, the identity of the second (ring-opened) isomer was not readily recognized. Initially, this species was assigned the propene cation structure,[11,13] but more recent results show that the trimethylene cation is a more likely assignment.[14,15] Unlike the cyclopropane study, a likely second structure for the methylenecyclopropane derivatives is suggested by the results of electron transfer reactions in solution. In the present study selective charge-transfer ion/molecule reactions were used for differentiating the isomeric ions because significant differences are expected between the recombination energies of the isomeric ions (corresponding to the ionization potentials of the



Propene Molecular Ion Trimethylene Cation

respective neutrals; *vide infra*). A group of reagent molecules were selected having ionization potentials varying over the full range of expected values, 6·9eV to 8·8eV.

EXPERIMENTAL

The ion/molecule reactions were carried out in the ion trap of a modified Nicolet FTMS-1000 Fourier transform mass spectrometer. The instrument contains a differentially pumped dual cell which permitted addition of the reagent and reactant on separate sides. The following conditions were used in these experiments: trapping voltage, 1·0V; electron energy, 15±1eV (FWHM); trapping time, 5 ms to 10 s; ionization duration, 5 ms; cell temperature, 25 °C. In order to examine the effect of ionization energy, the reactions with biphenylene were carried out at 10eV and 70eV as well. It is important to note that the electron energy has a broad energy distribution typical of heated filament sources. During electron impact ionization, ions were allowed to transfer between the two cells so that m/z 206^+ from the reactant could be isolated from its neutral precursor and allowed to react exclusively with the charge transfer reagent. However, the orifice between the two cells which allows ion transfer also permits the flow of some reactant neutral into the reagent cell and vice versa. This flow resulted in a reactant concentration that was ~1% of the reagent concentration in the reagent cell. This had a significant effect in some reactions as discussed later. As a precaution, ions not of interest, particularly those below m/z 178^+, were ejected from the cell by double resonance prior to reaction.

Ion intensities were monitored as a function of reaction time. Intensities at each time were normalized to the total ion intensity at that time. The intensity curves were fitted to exponential decay functions to evaluate the relative amounts of the isomeric ions. A single exponential decay was sufficient to fit the m/z 206^+ intensity decay for the reaction with ferrocene (Figure 1). Most other reactions were adequately described by a dual decay and an

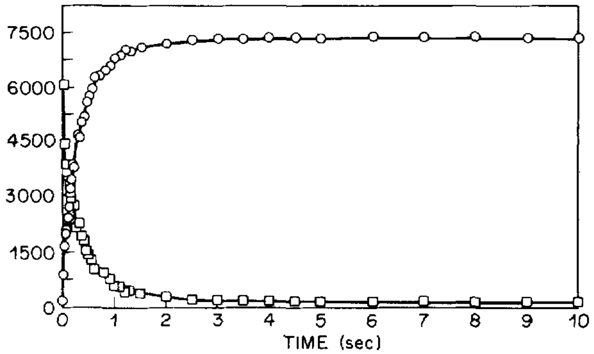


Figure 1. Intensity vs. time plot for m/z 206^+ generated by electron impact ionization of 1-(diphenylmethylene)cyclopropane during ion/molecule reaction with ferrocene. □ 206^+ ○ ferrocene$^+$

unreactive portion. A third exponential decay was necessary to account for the results observed with azulene, suggesting that three different species of m/z 206^+ react with the reagent at different rates. In some cases a back reaction was observed; accordingly the data were fitted with an additional component reflecting that rise. Overall, the observed decay curves were fitted to an equation of the form

$$\mathrm{d}I/\mathrm{d}t = \mathrm{A}e^{-\mathrm{B}t} + \mathrm{C}e^{-\mathrm{D}t} + \mathrm{E}e^{-\mathrm{F}t} + \mathrm{G}(1 - e^{-\mathrm{H}t}) + \mathrm{J} \qquad (1)$$

using a least squares fitting procedure in the ASYSTANT™ software package on an AT&T PC 6310 personal computer. A second or third exponential decay to fit the data was added only when the curve fitted badly with the simpler equation. The 'back reaction', when present, was fitted by the fourth term in equation (1). The fifth term was used when an unreactive fraction was present.

MATERIALS

2,2-Diphenyl-1-methylenecyclopropane was prepared by debromotosylation of 2,2-diphenyl-1-bromocyclopropane-1-hydroxymethyltosylate.[1] The isomeric substrate, 1-(diphenylmethylene)-cyclopropane was prepared by reaction of cyclopropyldiphenylphosphonium bromide with benzophenone.[16] These products were purified by high performance liquid chromatography using a 1/4″×25 cm column with Waters-Millipore-μ-Porasil as solid support and 2,2,4-trimethylpentane as eluent. The resulting purity of both compounds was found to be >99% by capillary gas chromatography/mass spectrometry. The charge transfer reagents employed were high grade commercial materials. They were used without further purification.

RESULTS

The molecular ions (m/z 206^+) from the reactants 2,2-diphenyl-1-methylenecyclopropane, *asym*-MCP, or 1-(diphenylmethylene)cyclopropane, *sym*-MCP, were reacted with a series of reagent molecules having ionization potentials ranging from 6·9 to 8·82eV. The extent of charge transfer reaction of m/z 206^+ with each reagent was monitored as a function of time, and the decay behavior was analyzed in terms of multiple-exponential decays and a nondecaying fraction as discussed in the Experimental Section. The pre-exponential factors and the constant were used to obtain the relative amount of each structural isomer for every reaction. Several different types of behavior was observed. With reagents of high IP either no or miniscule conversion was evident. For example, the reaction of m/z 206^+ (generated from *asym*-MCP) with *p*-xylene (IP = 8·37eV) leads to a rapid conversion of less than one tenth of the ions, with the remainder unreactive.

With a reagent of intermediate IP, substantial but less than complete conversion is observed leading to formation of the reagent ion and neutral reactant. This case is illustrated in Figure 2 for the reaction of m/z 206^+ (from *sym*-MCP) with biphenylene (IP = 7·56eV). Approximately one half of the initial population of m/z 206^+ reacts by charge transfer generating the biphenylene molecular ion (m/z 152^+). The decay of m/z 206^+ and the rise of m/z 152^+ can be described by a dual exponential function (*vide infra*). This type of behavior is typical for many of the reactions studied, but the extent of conversion depends upon the reagent.

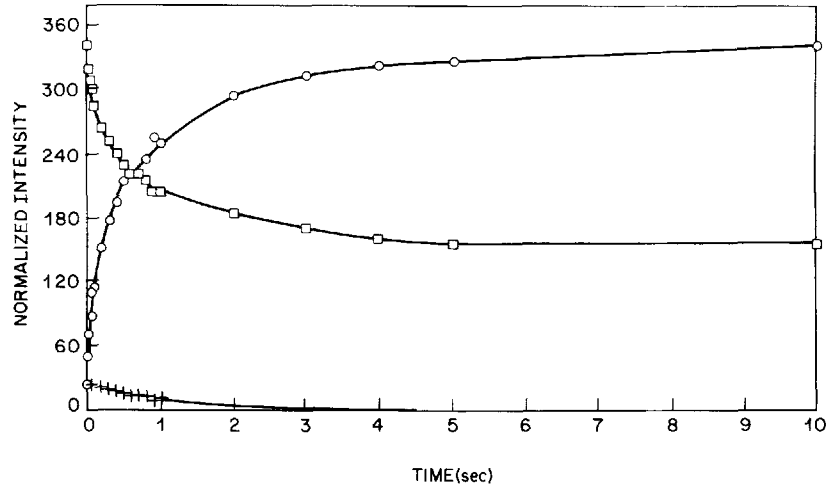


Figure 2. Intensity vs. time plot for *m/z* 206^+ and a fragment ion, *m/z* 128^+, $(M—C_6H_6)^+$, generated by electron impact ionization of 1-(diphenylmethylene)cyclopropane during ion/molecule reaction with biphenylene (formula weight 152). □ 206^+ ○ 152^+ + 128^+

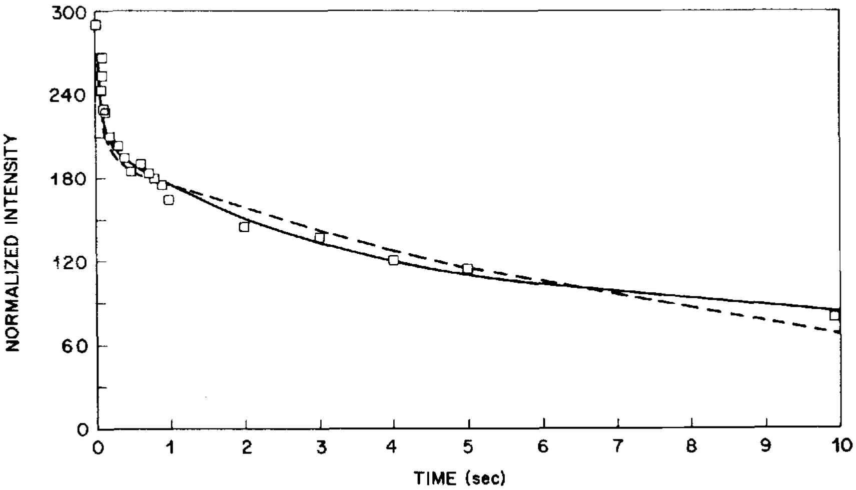


Figure 3. Intensity vs. time plot for *m/z* 206^+ generated by electron impact ionization of 1-(diphenylmethylene)cyclopropane during ion/molecule reaction with anthracene. The observed decay is simulated by single (—) and dual(——) exponential decay functions

For example, Figure 3 shows the experimental decay due to the reaction of *m/z* 206^+ from *sym*-MCP with anthracene. These data are presented together with the calculated fits using single and dual exponential decays. (The error bars are the size of the symbols.) Clearly, a dual decay function is necessary for a satisfactory fit. For reagents with IPs in the range 7·85 to 8·50eV, a complicating back reaction was observed. This behavior is illustrated in Figure 4 for the reaction of *m/z* 206^+ from *sym*-MCP with naphthalene. It is ascribed to the non-ideal separation of the substrate and reagent neutral molecules (*vide infra*).

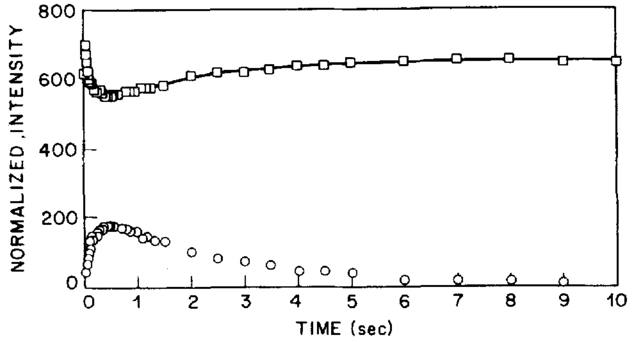


Figure 4. Intensity vs. time plot for *m/z* 206^+ (□) generated by electron impact ionization of 1-(diphenylmethylene)cyclopropane during ion/molecule reaction with naphthalene (○ $C_{10}H_8^+$)

The results of the ion/molecule reactions are summarized in Tables 1 and 2. The fraction of ions of *m/z* 206^+ which failed to react with a given reagent is designated as 'unreactive'; the fraction of reactive ions is divided into 'moderately reactive' and 'very reactive' according to their relative rates. The indication of a back reaction reflects regeneration of *m/z* 206^+ as noted above for naphthalene.

The effect of electron impact ionization energy was evaluated for the reaction with biphenylene. The kinetic evaluation of the different species was carried out at 10, 15, and 70eV. The results are presented in Table 3.

Table 1. Reaction of 1-(diphenylmethylene)cyclopropane molecular ion with selected electron donor reagents

Reagent	IP [eV]	Unreactive [%]	Moderately Reactive [%]	Very Reactive [%]	Back Rxn[a]
Ferrocene	6·90[b]	0	100	0	N
Azulene	7·41[c]	11[d]	54	34	N
Anthracene	7·47[b]	25	45	30	N
Biphenylene	7·56[c]	46	32	22	N
Acenaphthene	7·73[c]	66	19	15	N
Hexamethylbenzene	7·85[c]	68	21	11	Y
Naphthalene	8·10[c]	67	14	19	Y
p-Xylene	8·37[b]	87	5	8	Y
m-Xylene	8·50[b]	80	0[e]	20	Y[f]
Toluene	8·82[b]	96	0[e]	4	Y[f]

[a] Charge transfer of the reagent cation to diphenylmethylenecyclopropane to form the open cation.

[b] H. M. Rosenstock, K. Drakl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, 6, (1977).

[c] R. D. Levin and S. G. Lias, *Nat'l. Stand. Ref. Data Ser., Nat'l. Bur. Stand. (U.S.)*, 71 (1982).

[d] Amount of slowly reacting species. There was no unreactive species.

[e] Cannot be differentiated from the unreactive fraction.

[f] This is normal charge transfer reaction.

Table 2. Reaction of 2,2-diphenyl-1-methylenecyclopropane molecular ion with selected electron donor reagents

Reagent	IP [eV]	Unreactive [%]	Moderately Reactive [%]	Very Reactive [%]	Back Rxn[a]
Azulene	7·41[b]	7[d]	78	15	N
Biphenylene	7·56[b]	41	26	33	N
Acenaphthylene	7·73[b]	52	5	43	N
Hexamethylbenzene	7·85[b]	49	10	41	Y
Naphthalene	8·14[b]	75	3	22	Y
p-Xylene	8·37[c]	86	4	10	Y
m-Xylene	8·50[c]	92	0[e]	8	Y[f]

[a] Charge transfer of the reagent cation to methylenediphenylcyclopropane to form the open cation.

[b] R. D. Levin and S. G. Lias, *Nat'l. Stand. Ref. Data Ser., Nat'l. Bur. Stand. (U.S.)*, 71 (1982).

[c] H. M. Rosenstock, K. Drakl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, 6 (1977).

[d] Amount of slowly reacting species. There was no unreactive species.

[e] Cannot be differentiated from the unreactive fraction.

[f] This is a normal charge transfer reaction, observed upon ionization of *m*-xylene and interaction with methylenediphenylcyclopropane as electron transfer reagent.

Table 3. Effect of electron impact ionization energy on distribution of isomers

Reactant	Electron Energy [eV]	Unreactive [%]	Moderately Reactive [%]	Very Reactive [%]
Diphenylmethylenecyclopropane, **4**	10	52	21	27
	15	46	32	22
	70	31	42	27
Methylenediphenylcyclopropane, **3**	10	59	27	14
	15	41	26	33
	70	15	11	74

For comparison with previous work on diolefin dimers, particularly dicyclopentadiene and derivatives, the ions of m/z 206^+ from *sym*-MCP were reacted with their precursor. The abundances of very reactive, moderately reactive, and unreactive ions (13%, 23%, and 65%, respectively) fall into the general range observed with reagents of high IP.

DISCUSSION

The charge transfer reactions between the ions generated from methylenecyclopropane derivatives and several appropriate electron donors show several unusual features in addition to the existence of different isomeric ions. We will discuss the nature of the ions formed, their recombination energies, the factors affecting their populations, and the nature of an unusual back reaction.

Structural assignments

Based upon the CIDNP results obtained in solution, two structure types must be considered for the ions of *m/z* 206^+: the molecular (vertical) ions and a ring-opened, nonvertical ion (TMM^+), **1**. The latter species is distinguished from either vertical ion by different electron recombination energies (corresponding to different ionization potentials of the respective neutrals). For *asym*-MCP, an ionization potential similar to that of 1,1-diphenylcyclopropane, (IP = 8·50eV), is expected,[17] whereas the IP of *sym*-MCP should be similar to that of 1,1-diphenylethylene (IP = 8·00eV).[18] In contrast, the diradical neutral derived from **3** is expected to have a substantially lower IP, possibly similar to the value for phenylmethyl radical (IP = 7·20eV).[19]

Charge transfer ion/molecule reactions have been used to determine the ionization potential of molecules;[20–22] their application to differentiate isomers should be straightforward. However, the systems discussed here gave peculiar results with several reagents. For example, in the charge transfer reaction of *m/z* 206^+ (generated from *sym*-MCP) with naphthalene, N, the intensity of *m/z* 206^+ decreased initially, but then increased again. N^+ showed complementary behavior (Figure 4). The initial decay is assigned to the formation of N^+ by charge transfer from *m/z* 206^+ (cf. reaction 2). The subsequent partial recovery of intensity arises from the apparent back reaction, i.e. N^+ reforms *m/z* 206^+ (reaction 3).

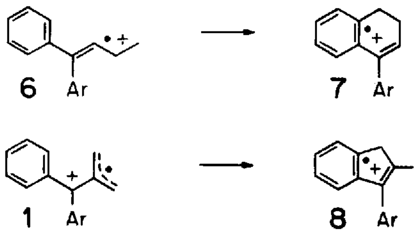
$$206^+ + N \rightarrow N^+ + 206 \tag{2}$$

$$N^+ + 206 \rightarrow 206^+ + N \tag{3}$$

This unusual observation is ascribed to the presence of a small fraction (~1%) of (neutral) substrate molecules (*asym*-MCP or *sym*-MCP) in the trapped ion cell with the reagent. The observed rate of the back reaction (3) is considerably lower than the rate of the initial charge transfer reaction (2), in keeping with the lower concentration of the substrate. In principle, a back reaction should decrease the efficiency of conversion resulting ultimately in a constant intensity of the ions, thereby enabling an equilibrium measurement. However, the system discussed here is complicated by the fact that the back reaction results in the formation of TMM^+, **1**, resulting from an isomerization of the closed structure. (This observation will be discussed in more detail later). As a result, normal equilibrium measurements to obtain ionization potentials are not applicable in this system. Instead, reagents with a range of ionization potentials were selected in an attempt to bracket the ionization potentials of the *m/z* 206^+ isomers. Furthermore, the back reaction ruled out normal bracketing methods. Instead, the variation of the intensity of *m/z* 206^+ with time was fitted to a multiple exponential decay function as described in the Experimental Section. The structural isomers were then assigned on the basis of their reactivities.

The decay behavior of the ions of *m/z* 206^+ in the reaction with biphenylene (Figure 2) and anthracene (Figure 3) is noticeably different. Nevertheless, both can be described by the same type of decay functions. Attempts to fit the decay of *m/z* 206^+ from *sym*-MCP to a single exponential decay function and an unreactive portion resulted in a far from satisfactory fit (cf. Figure 3); only a dual exponential decay function and an unreactive portion provided an acceptable fit to the data.

The unreactive fraction was assigned to the species of lowest recombination energy, TMM^+, **1**, but two additional decay components remained. This was true as well for the alternative substrate, *asym*-MCP. In either case, the species decaying with a moderate reaction rate becomes unreactive with *m*-xylene (cf. Tables 1, 2). This behavior is commensurate with the



estimated recombination energy of the closed structures (**2** or **5**); accordingly, the moderately reactive ions are assigned as vertical ions in which the cyclopropane ring remains unaffected.

The recombination energies of the moderately reactive ions are also consistent with rearranged ions having dihydronaphthalene or indene structures. Both **7** and **8** are, in essence, diphenylethene ions with estimated recombination energies similar to **2**. Nevertheless, these structures were eliminated as candidates. Their involvement would require a 100% efficiency of ring cleavage, which is without precedent in either cyclopropane[11,12] or dicyclopentadiene.[23]

The third and most reactive component undergoes charge transfer even with toluene (IP=8·82eV). Its reaction rate exceeds the Langevin (collision) rate by roughly an order of magnitude. At higher ionization energies (70eV) the very reactive ion is dramatically increased in abundance when generated from *asym*-MCP and probed with biphenylene. On the other hand, the abundance of this ion is essentially independent of ionization energy when generated from *sym-MCP. The pronounced difference in their response to ionization at low and high energies sets apart asym*-MCP and *sym*-MCP most clearly. The presence of the very reactive fraction constitutes a major problem for the interpretation of these data. This behavior cannot be ascribed simply to ion loss from the cell; this very reactive component is the only one which reacts with toluene and *m*-xylene with the simultaneous formation of the corresponding molecular ions. Internal vibrational energy should have only a slight effect on the rate of charge transfer;[24] but not the nearly order of magnitude effect observed here. The explanation is difficult; there have not been extensive studies on charge-transfer reactions involving reaction partners of this size. We tentatively suggest two explanations for the very reactive species. A closed structure in a comparatively long-lived electronically excited state, possibly a quartet state, may explain the apparent high recombination energy. An alternative explanation involves a ring-opened ion (**6**) which lacks allylic or benzylic stabilization. Such an ion occupies a larger volume than the other reactant ions, possibly resulting in a larger reaction cross section. This species may be expected to become more prominent at higher ionization energies, as is observed for at least one of the reagents (cf. Table 3).

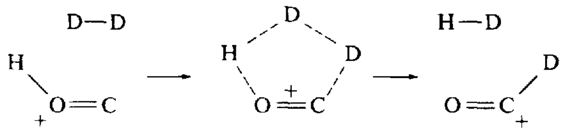
Recombination energies

The least reactive species, the bifunctional ion of structure **1**, reacts rapidly with ferrocene but is unreactive toward anthracene. Its reaction with azulene is very slow, with an efficiency of 0·03–0·07. This suggests that the driving force may be, in part, the nonequilibrium reaction due to a lack of the neutral reaction partner (corresponding to uncharged **1**) for the reverse reaction. Thus, the recombination energy of species **1** is assigned as approximately equal to the IP of azulene, 7·4 ± 0·05eV. This value lies slightly above that of our estimate (7·2eV) but clearly below the values estimated for the vertical ionization potentials or the recombination energies of the rearranged ions, **7** and **8**.

The moderately reactive species are assumed to be the molecular ions. For both *asym*-MCP and *sym*-MCP, the IP must lie between those of *p*-xylene and *m*-xylene, 8·45 ± 0·05eV. This value is comparable to our estimated ionization potentials of 8·5eV and 8·0eV, respectively. The most reactive species has a recombination energy that appears to lie higher than the ionization potential of toluene, 8·82eV.

Isomerization

The observed fraction of TMM^+, **1**, increases with increasing ionization potential of the reagent, coincident with a decrease in the amount of MCP^+ (MCP^+ will be used as a generic term for both the closed *sym*-MCP^+ and closed *asym*-MCP^+). Since the initial population prior to reaction must be independent of reagent, the isomerization of MCP^+ to TMM^+ must be catalyzed by the reagent. This is supported by the 'back reaction' which involves catalysis of the isomerization of MCP to TMM by the reagent cation. Catalytic isomerization in the gas phase is not without precedent. For example, the reaction of HOC^+ with D_2 led to the formation of DCO^+.[25]



For the methylenecyclopropane derivatives discussed here, the reaction of the closed molecular ion, MCP^+, can follow two pathways, charge-transfer (4a) to form the reagent cation or isomerization (4b) to form the nonvertical ion, TMM^+:

$$MCP^+ + \text{reagent} \rightarrow \text{reagent}^+ + MCP \qquad (4a)$$

$$\rightarrow TMM^+ + \text{reagent} \qquad (4b)$$

The occurrence of the charge-transfer reaction depends on the ionization potentials of the two reactants but the formation of TMM^+ is governed by a more complicated reaction surface. This is illustrated in Figures 5 and 6 for the reactions of four reagents with MCP^+. The relative energies for the reactants and most products, both neutral and ionic, are well known or have been determined in this study. The energies of the ion/molecule complexes and the energy of $TMM^+$are not known. Suggested values are indicated by dashed lines as a guide to the expected general behavior. The relative heights of the isomerization barrier and the final products, TMM^+ and reagent, cannot be determined from this study. The following discussion assumes that the isomerization barrier lies at higher energy and thereby is the rate-limiting step in the reaction. If it were to lie at lower energy, there would be an unreasonably small destabilization on going from the associated MCP^+ to the transition state for isomerization. In addition, if the isomerization barrier were lower, then TMM^+ would react with azulene to produce A^+. This reaction is not observed.

A comparison between the reactions of MCP^+ with the reagent naphthalene (N) and azulene (A) illustrates substantially different behavior (Figure 5). For the reaction with N, formation of TMM^+ was observed from both MCP^+ and N^+. This observation requires that the energy of the products and the isomerization barrier lie below the energies of both sets of reactants. In contrast, for the reaction with azulene, the energy of the A^+ and MCP lies

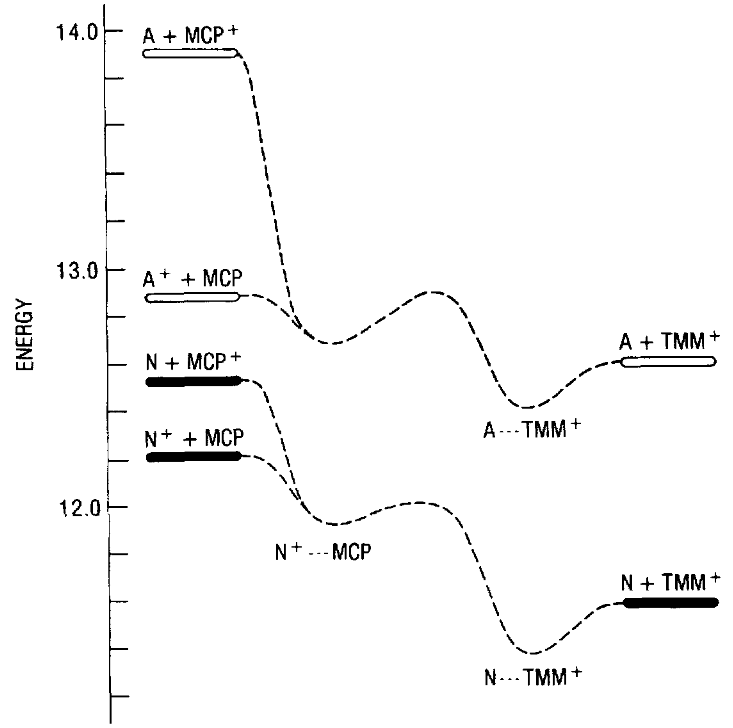


Figure 5. Schematic representation of the net isomerization of vertical methylenecyclopropane ion (MCP$^+$) in the presence of naphthalene (N) and azulene (A)

~0·03eV below the energy of the isomerization barrier (*vide infra*). This fact coupled with the entropy constraints for isomerization favors the charge-transfer reaction (4a) relative to the isomerization process (4b). Thus the reaction with A is adequate to evaluate the true initial population of TMM$^+$.

The back reaction, i.e. the apparent regeneration of m/z 206$^+$ from the reagent cation, occurs for reagent molecules with IP $>$ 7·8eV; this reaction can be explained only if it results in the formation of TMM$^+$. The energy/reaction coordinate plots for reaction of MCP$^+$ with acenaphthene (B) and hexamethylbenzene (H) are compared in Figure 6. Based on the observed lack of a back reaction for B$^+$, the isomerization barrier must lie higher in energy than the pair MCP and B$^+$ ($>$7·73eV above nonassociated MCP and B). Likewise, since H$^+$ does exhibit the back reaction, the isomerization barrier must lie $<$7·85eV above the energy of nonassociated MCP and H. Thus, the barrier for isomerization of TMM$^+$ to MCP$^+$ lies 7·8 ± 0·1eV above nonassociated MCP and reagent.

This barrier appears to lie below the energy of MCP$^+$ (cf. Figures 5 and 6); thus spontaneous isomerization to TMM$^+$ might be expected. However, the isomerization barrier represents the transition state for isomerization of an ion associated with a reagent molecule. The association energy lowers the barrier to a value below the energy of nonassociated MCP$^+$. Thus the energy for isomerization is supplied by the association energy plus the energy from charge transfer to the reagent. Without that extra energy, MCP$^+$ is quite stabe as evidenced by its large fraction of the 206$^+$ population (Tables 1 and 2). The associated MCP$^+$, which lies at the minimum between the reactants and the isomerization barrier, is more accurately

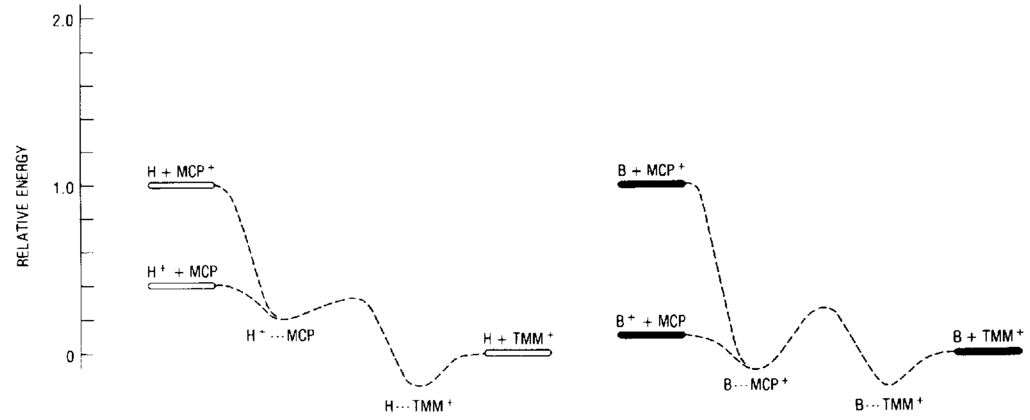


Figure 6. Reaction coordinates for the interactions of MCP$^+$ with hexamethylbenzene (H, left) and acenaphthene (B, right). Since the energy of the pair, H$^+$ plus MCP, lies appreciably above the pair, H plus TMM$^+$, electron transfer and ring opening can occur in the association complex. Conversely, as B$^+$ plus MCP is nearly isoenergetic with B plus TMM$^+$ the association energy is not sufficent to overcome the barrier for this process

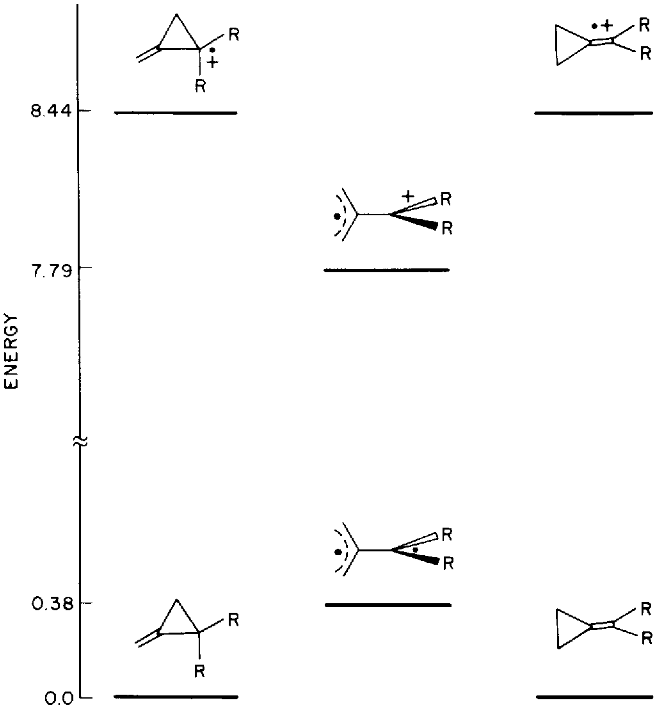


Figure 7. Relative energies (eV) of $C_{16}H_{14}$ neutrals and singly charged ions

described as MCP bound to the reagent cation. For the higher IP reagents, *m*-xylene and toluene, the minimum represents MCP$^+$ associated with the reagent. Without assocation, the isomerization barrier must lie above the energy of MCP$^+$. Thus the effects of lowering the energy by association are clearly seen.

The energy of TMM^+ cannot be determined directly from these experiments. Its value is limited by the following considerations. The energy of neutral TMM must lie higher than the energy of either *sym*- or *asym*-MCP. The energy of TMM^+ plus the reagent is assumed to lie below that of the isomerization barrier. Given these constraints, the energy of TMM must be higher than the MCPs by 0·17 ± 0·17eV and the energy of TMM^+ must be higher than the MCPs by 7·79 ± 0·17eV. The relative energies of these isomers are illustrated in Figure 7.

Isomer populations

The true initial populations of TMM^+ are determined for the reaction with azulene (*vide supra*). These values are 7% and 11% for *asym*-MCP and *sym*-MCP, respectively. Obviously, there is little difference in the extent to which these two molecules undergo ring-opening upon electron impact in the gas phase. In marked contrast one-electron oxidation in solution results in ready ring-opening of *asym*-MCP whereas *sym*-MCP remains closed.[7] This difference between gas phase and solution may be due to the higher efficiency with which excess energy is dissipated in solution and may be further accentuated by different solvation energies for different structure types. The fractions of closed (moderately reactive) and 'hot' (very reactive) species were also determined for the reaction with azulene. For *sym*-MCP, the abundances are 54% and 34%, respectively, whereas for *asym*-MCP, the abundances are 78% and 15% respectively.

Comparison to related systems

The driving force for the ring opening of the cyclopropane systems lies in their strain energy and in the presence of an allylic cyclopropane bond. The formation of an allylic radical and a doubly benzylic cation along with the release of strain energy more than offsets the energy required to sever the bond. However, ring opening is not limited to cyclopropane systems giving rise to stabilized radical cations. The cyclopropane cation itself has been found to undergo ring opening in the gas phase.[11-15] The observed reactions are consistent with the presence of cyclopropane molecular ion and of a ring-opened isomer, trimethylene radical cation. Our results parallel that finding: two isomers are present which represent the ring-closed and ring-opened ions of the cyclopropane derivatives. The ring-opening of cyclopropane ions, like the ions in this study, was observed to vary with ionization energy. The ion population in the cyclopropane study was probed by ion/molecule reactions to determine the fractions of each isomer. However, based upon the results of our present study, this type of probe can affect the ion populations through isomerization to the more stable form. Thus the abundances may be distorted when an ion/molecule reaction is utilized to either generate an ion, e.g. by charge transfer, [14] or probe its structure, e.g. by proton transfer.[11-15] This caveat is applicable for all systems with low barriers to isomerization. In any of these systems, the rearranged or ring-opened isomer may be formed by two different processes, and its fraction, therefore, will be larger than that caused by the initial ionization process alone.

A similar situation was encountered in our previous study[23] of the ions derived from [4+2]dicyclopentadiene and derivatives. In that study the isomer populations were probed by reacting the ions with their precursors. In the light of the current study we note that the abundance of the ring-opened singly linked ions was probably overestimated. A similar reaction between *sym*-MCP and its 'molecular' ion indicated the presence of 65% ring-opened isomer (TMM^+), a value considerably higher than the 11% derived from the corresponding reaction with azulene as an electron transfer reagent.

SUMMARY

Ions of *m/z* 206^+ derived from electron impact on *sym*- and *asym*-MCP were reacted with reagents having ionization potentials from 6·9 to 8·83eV. A fraction of the ions are unreactive except with two reagents having the lowest ionization potential. These ions are assigned a trimethylenemethane structure, **1**, with an IP equal to 7·41 ± 0·05eV. A second fraction of ions are reactive with all but two reagents having the highest IP. These ions are assigned the structure of the corresponding molecular ion with an IP equal to 8·44 ± 0·05eV. A third fraction of ions are reactive with all the reagents used in this study. The identity of this ion is uncertain but is ascribed to a long-lived electronically excited species. The observed abundance of each structure varies systematically with the IP of the reagent. Isomerization within the ion/molecule complex is postulated to explain the abundance variation. The 'true' abundances are assigned based upon reaction with the lowest IP reagent, azulene, which discriminates among the three species. The abundances for the first, second, and third fractions are: 11%, 54%, and 34%, respectively, for *sym*-MCP and 7%, 78%, and 15%, respectively, for *asym*-MCP.

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