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Bicyclobutonium ion versus cyclopropylcarbinyl cation chemistry: the cycloaddition reaction with ethene in the dilute gas phase

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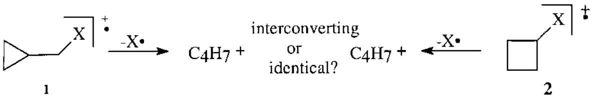
ABSTRACT: The $C_4H_7^+$ cations were formed from cyclopropylcarbinyl, cyclobutyl and homoallyl chlorides via chloride atom loss from the radical cations in a chemical ionization source. Their structures were probed on a short time-scale (of the order of 10^{-6} s) as a function of internal energy by utilizing collisionally activated dissociation with tandem mass spectrometric methods. The results show that the radical cations of cyclopropylcarbinyl and homoallyl chlorides generate primarily the cyclopropylcarbinyl cation, **3**, whereas the radical cation of cyclobutyl chloride generates a substantial amount of bicyclobutonium ion, **4**. Ion **4** reacts with nucleophiles via multiple competing reaction pathways, unlike **3**. Ion **3** undergoes a cycloaddition reaction with ethene to generate the cyclopentylcarbinyl cation. Ion **4**, although reactive with ethene, does not generate, to any appreciable degree, the cyclopentylcarbinyl cation. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: bicyclobutonium ion; cyclopropylcarbinyl cation; ion structures; ion–molecule; reactions; tandem mass spectrometry

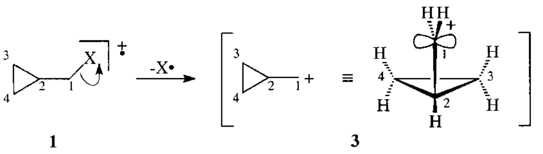
INTRODUCTION

The structures and isomerizations of the $C_4H_7^+$ cations resulting from cyclopropylcarbinyl, **1**, and cyclobutyl substrates, **2**, [Eqn. (1)] have been the focus of more studies than any other cationic system with the singular exception of those from 2-norbornyl substrates.[1]



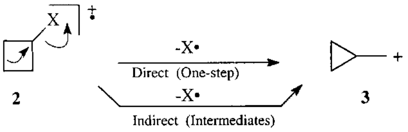
(1)

Early interest in these systems stemmed from the surprising observation that neutral cyclopropylcarbinyl and cyclobutyl substrates solvolyze at unexpectedly high rates to cations.[1–4] The rapid solvolysis of cyclopropylcarbinyl substrates is a result of σ-bond participation from the ring, presumably generating a symmetrically stabilized cyclopropylcarbinyl cation, **3** [Eqn. (2)].[3,4]



(2)

The enhancement in the rate of solvolysis of cyclobutyl substrates may also be the result of σ-bond participation from the ring in the generation, either directly or indirectly, of **3** [Eqns (3) and (4)].[3,4]



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(4)

Is the cyclopropylcarbinyl cation the first formed ion in the solvolysis of cyclobutyl derivatives? Majerski, *et al.*[5] reported significantly reduced H–D label scrambling in ions that come from isotopically labeled cyclopropylcarbinyl substrates compared with those that arise from cyclobutyl derivatives. The interpretation was that the cyclopropylcarbinyl derivatives solvolyze directly to **3**, whereas the cyclobutyl derivatives solvolyze initially to ions with a cyclobutyl structure.

In contrast, orbital symmetry considerations, coupled with measurements of relative solvolysis rates for

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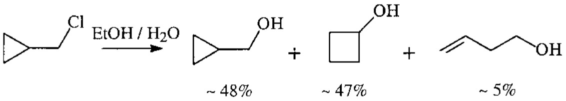
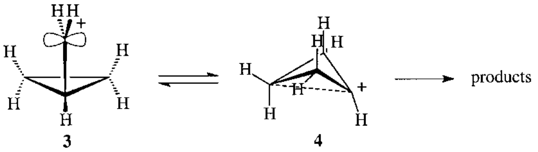
substituted cyclobutyl derivatives, suggest that a substantial, if not quantitative, amount of the cyclopropylcarbinyl cation is formed directly from cyclobutyl substrates.[6]

Although there is disagreement regarding the nature of the ions formed initially upon solvolysis, it is clear that, upon solvent capture, mixtures of neutral products result. Roberts and Mazur[7] showed that cyclopropylcarbinyl chloride reacts with ethanol-water to give the product mixture shown in equation Eqn. (5). The analogous reaction starting with cyclobutyl chloride gave similar products.[8]



(5)

Brown[9] postulated that the cyclopropylcarbinyl cation is in rapid equilibrium with the classical cyclobutyl cation, both of which react with solvent to give products. In contrast, Roberts and co-workers,[10–13] posited that the observed products result from a common intermediate, the bicyclobutonium ion, **4**, which is the prototypical 'non-classical' carbocation. Furthermore, they postulated that **3**, from either cyclopropylcarbinyl or cyclobutyl substrates, isomerizes to **4** [Eqn. (6)], which is then attacked by a nucleophile at any of the three sites that bear cation character, leading to the cyclobutyl, cyclopropylcarbinyl, and homoallyl derivatives.



(6)

A major difficulty in understanding the ionic intermediates involved in solvolysis reactions is that the nature and extent of ionic interconversions is inferred from the products formed upon nucleophilic attack on the intermediate(s). However, direct observation of the ions themselves, generated as long-lived intermediates in super acid media and analyzed by various NMR techniques, has afforded additional insight.

The outcome of NMR investigations of these systems in superacid media does not support Brown's interpretation. Olah *et al.*[14] reported that cyclopropylcarbinol and cyclobutanol on reaction with SbF_5–SO_2ClF at −80 °C gave identical ^1H and ^{13}C NMR spectra. The NMR results coupled with those using labeled precursors[15] led to the conclusion that there is no significant participation by the classical cyclobutyl cation. Evidence generated by the NMR deuterium isotopic perturbation technique led Saunders and Siehl[16] to postulate that **4** is the major species present in an equilibrating mixture and that **3** serves as a transition state between the bicyclobutonium forms. In 1984, Brittian *et al.*[17,] however, generated stereoisomers of trideuterated cyclopropylcarbinyl cations in super acid and demonstrated via NMR that **4** is indeed in equilibrium with a less abundant isomer, presumably **3**. Thus, some quantity of **3** co-exists and interconverts with **4**, a finding that is supported by related work.[16–22] By comparing experimental and calculated shifts to make a quantitative assessment, the **3:4** mole ratio was determined to range from 25:75 at −61 °C to 16:84 at −132 °C.[23,24] Boltzmann population analysis based on these data showed that **4** is 0.20 kJ mol^{-1} more stable than **3**.

NMR studies deal with cations that are relatively long-lived, whereas those formed by solvolysis are short-lived, solvated species. In both cases, the ions formed are solvated and experience numerous collisions. Mass spectrometry, in contrast, deals with the formation of ions in the solvent-free gas phase under conditions where the ions may be sampled at short times after formation, and where the number of collisions with a selected target can be controlled. The opportunities of mass spectrometry motivate the direct observation of the $C_4H_7^+$ cations in the dilute gas phase. The purpose of the research reported here was to compare the results with those obtained in solution and to determine whether the two isomeric precursors, cyclopropylcarbinyl and cyclobutyl, produce the same initial ionic species.

Cyclopropylcarbinyl, cyclobutyl, and homoallyl chlorides, when ionized to radical cations in a high-pressure chemical ionization source, produce $C_4H_7^+$ species via Cl radical loss. We formed the $C_4H_7^+$ ions with differing internal energy and analyzed their product-ion mass spectra produced by using collisional activation. We also compared the gas-phase, bimolecular reactivities of the $C_4H_7^+$ with neutral methanol and ethene to learn more about **3** and **4**. The logic of using ethene as a probe is based on the theoretical investigations of Cramer and Barrows,[25] who predicted that ethene will undergo a cycloaddition with **3** but not with **4**. This work thus provides an experimental test for the applicability of ethene as a selective reagent for the cyclopropylcarbinyl cation.

EXPERIMENTAL

CAD mass spectrometry. All collisionally activated dissociation (CAD) mass spectra were obtained by using a Kratos MS50-TA tandem mass spectrometer of EBE design, which consisted of a high-resolution mass spectrometer (MS-1) of Nier–Johnson design followed by an electrostatic analyzer (ESA-2 as MS-2).[26] Ions formed in the Kratos Mark-V CI (chemical ionization) source were accelerated to a kinetic energy of 8 keV and were mass selected at a mass-resolving power of 2500–3500 (10% valley definition) by using MS-1. The ions were activated by 8 keV (laboratory frame) collisions with helium gas (UHP grade) in the collision cell located

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between MS-1 and ESA-2; sufficient helium was added to suppress the ion beam by 50%. ESA-2 was scanned to give the CAD spectrum of the resulting fragment ions. In a typical CAD experiment, 20–40 scans were acquired and then signal averaged. Relative abundances were calculated from the measured peak heights for all ions in the spectrum, fragment and precursor, with the latter set to 100%. The precision for all peak heights reported was approximately 5% relative as determined by replicate experiments. The peak heights of replicate experiments were averaged; these results spanning all reported CAD processes are reported in Table 1.

Ion formation. All ions were prepared in the CI source that was operated at a temperature of 100 °C and at an electron energy of 280 eV. Samples and reactants were introduced through a custom-built glass reservoir probe such that total sample pressure was 1×10^{-6} Torr (1 Torr = 133.3 Pa) as registered on the external pressure gauge on the source high-vacuum manifold. Gaseous CS_2, which served as both a buffer and charge-exchange gas, was admitted through a custom-built heated glass inlet system into the CI source such that the pressures external to the source were as high as 1×10^{-4} Torr. (An external pressure of 1×10^{-4} Torr, measured by a Bayard–Alpert vacuum gauge mounted on the vacuum manifold outside of the ion source, corresponded to an internal source pressure of $\approx$0.2 Torr, as determined by a custom-built pressure probe, basically a sample inlet probe with a thermocouple-element vacuum gauge mounted on it.) Furthermore, the residence time for ions in the CI source was a few microseconds.

The ions of interest were generated either by ion–molecule reactions or from the radical cations of the appropriate chloride via chloride atom loss. The pressure of the CS_2 bath gas was used to modulate the internal energy of the ions via collisional cooling.[27–31]

Table 1. CAD production, the relative abundances (%) of CAD fragments as a function of ion internal energy[a]

Source	Energy[b]	*m/z* 25	26	27	28	29	37	38	39	40	41	49	50	51	52	53	54
Cyclopropylcarbinyl chloride	L	0.8	4.6	16.8	3.7	7.7	2.7	5.0	20.3	1.7	1.5	2.0	8.1	7.6	2.4	8.6	7.0
	H	0.8	4.8	18.7	4.3	8.8	2.7	5.3	21.9	1.4	0.9	1.9	7.6	6.8	1.9	7.1	5.0
Cyclobutyl chloride	L	2.8	11.0	11.3	6.1	4.8	3.3	9.1	17.3	2.1	1.1	1.7	7.9	6.9	1.7	8.1	5.4
	H	2.9	12.1	13.8	6.7	4.5	3.6	8.9	17.2	1.9	0.8	1.9	7.7	5.2	1.8	6.8	4.5
4-chloro-1-butene	L	0.7	4.7	19.0	3.8	11.0	2.8	5.3	21.8	1.8	0.8	1.8	7.2	6.5	1.8	7.5	4.1
(homoallyl chloride)	H	0.8	4.3	17.8	3.7	8.9	2.6	4.9	20.6	1.7	0.9	1.9	7.8	7.2	2.3	9.2	5.8

		m/z 27	29	39	41	43	45	53	55	57	58	71	72
Cyclopropylcarbinyl + methanol	L	4.6	4.8	3.5	5.3	3.0	39.0	1.3	8.1	8.6	7.3	7.3	2.3
Cyclobutonium + methanol	L	3.5	3.5	3.1	4.0	2.4	37.6	1.1	14.8	11.5	5.3	9.7	1.5

		m/z 27	29	39	41	43	50	51	53	55	63	65	67	68	77	79	81	82
Cyclopropylcarbinyl +	L	4.8	2.3	9.3	12.0	1.4	1.4	2.0	4.5	33.9	0.7	2.0	14.0	1.8	1.5	1.8	2.1	5.0
ethylene	H	4.2	2.1	9.3	11.7	1.4	1.4	2.1	4.7	33.5	0.6	2.0	14.4	1.6	1.3	1.9	2.2	5.3
Cyclobutonium + ethylene	L	4.3	2.5	10.0	12.6	1.3	1.3	2.3	4.5	36.1	0.6	1.6	12.3	1.3	1.0	1.5	2.1	4.0
	H	3.8	1.9	9.0	12.1	1.3	1.0	2.0	3.8	45.1	0.5	1.2	10.6	0.6	1.0	1.4	2.0	2.7
Cyclohexyl chloride	L	3.4	1.9	8.5	11.6	0.8	1.3	2.3	4.5	28.2	0.7	1.3	19.3	0.8	2.5	4.1	5.0	5.3
	H	3.9	2.2	9.1	12.0	0.6	1.2	1.9	4.5	22.6	0.6	1.7	19.6	0.5	2.6	4.1	5.0	6.8
Cyclopentylcarbinyl chloride	L	3.0	1.8	8.3	11.4	0.5	1.1	1.9	4.0	43.3	0.3	1.5	14.9	0.3	1.9	2.8	3.0	1.5
	H	3.7	2.1	10.1	13.3	0.5	1.1	2.0	4.4	33.6	0.5	1.5	14.4	0.8	1.9	3.1	3.6	3.6
3-Chloro-1-hexene	L	3.7	2.5	8.0	12.2	0.9	0.9	2.3	4.0	46.2	0.4	1.6	11.6	0.8	1.0	1.2	1.8	2.9
(*n*-propylallyl chloride)	H	3.6	2.1	8.3	11.9	0.7	0.7	2.1	4.6	42.6	0.4	1.4	13.0	1.1	1.4	1.8	1.8	2.9
6-Chloro-1-hexene	L	4.1	2.4	8.4	11.3	0.9	1.2	2.1	3.9	39.1	0.3	1.5	11.6	1.8	1.2	1.8	2.4	4.2
	H	4.2	2.4	9.1	12.4	1.3	1.0	1.9	4.2	38.3	0.4	1.6	11.8	2.6	1.4	1.6	2.6	4.5
1-Chloro-1-methylcyclopentane	L	4.3	2.4	10.9	13.8	0.5	1.2	2.2	4.4	29.4	0.5	1.7	15.6	0.5	1.7	3.3	4.4	3.3
	H	4.3	2.4	10.5	14.0	0.6	1.2	2.2	4.4	28.5	0.4	1.3	15.8	0.6	1.8	3.5	4.8	3.6

[a] Abundances are derived from measured peak heights and normalized relative to the main beam (100%).

[b] ‘L’ and ‘H’ designate ions formed for low and high internal energies, respectively (see Experimental section).

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All chemicals were obtained from Aldrich Chemical (Milwaukee, WI, USA) and used without further purification.

CAD Spectra as a function of internal energy. Changes in the structure or composition of analyte ions that originate from the various precursors were probed by using tandem mass spectrometry, where the ion structure was evaluated as a function of internal energy by an established technique.[27–31] Via this technique, the internal energy was varied by generating the analyte cations within a high-pressure, chemical ionization source in the presence of an inert bath gas. The bath gas, CS_2, which also served as a charge exchange gas, collisonally stabilized the analyte ion of interest once formed. At the maximum bath-gas pressure, these two processes formed ions with low average internal energy. As the pressure of the bath gas was reduced, the extent of direct ionization increased and the degree of collisional stabilization of the analyte ion decreased, and, consequently, the average internal energy of the produced ions increased. The CAD spectra of the analyte ion were collected in a set of experiments, where in each successive experiment the CS_2 pressure was incrementally reduced. The evaluation of spectral changes as a function of bath gas pressure allowed the study of structural or compositional change as a function of internal energy.

At the maximum bath pressure (0.2 Torr, internal) ions would experience an average of about two collisions per microsecond before leaving the source. Higher bath gas pressures did not yield any additional changes in the CAD spectra of the ions and adducts. By analogy with other systems,[32] the ions and adducts produced in this study would be thermolyzed by <10 collisions with the CS_2 bath gas. This indicates that the source residence time involved in ion formation is <5 μs.

With no CS_2, the ions produced have the highest internal energy; and with CS_2 at an external pressure of 1×10^{-4} Torr (internal pressure of ≈ 0.2 Torr), ions of the lowest internal energy were produced. These sets of ions are designated ‘H’ and ‘L’, respectively, in Table 1.

Spectral comparison method. The differences in the CAD spectra from these experiments are not characterized by the presence or absence of distinct fragment ions, but rather are reflected in differences in the overall patterns of fragment ion abundances. To compare quantitatively the CAD spectra for ions at differing internal energies and/or origins, we used a spectral comparison method[33,34] where the *m/z* values of selected *n* fragment ions were used to define a basis over an *n*-dimensional space. Each CAD spectrum was represented as an *n*-dimensional vector where the elements were the peaks heights at the corresponding *m/z* values. Colinearity defined similarity, even in the presence of different scale factors. The angle between the vectors, θ, which we termed the divergence angle, was processed from the vector dot-product and was used as the measure of similarity. An angle of zero indicated that the two spectra being compared were identical. Angles $>5°$ were considered large enough to allow us to conclude with confidence that the spectra arose from either a different structure, a different mixture of structures or a different composition of a mixture with common structures. Angles $<5°$ were considered identical within experimental error (based upon repeated experiments on the same ions under identical conditions), and probably represented the formation of common structures or mixtures of structures.

RESULTS AND DISCUSSION

CAD spectra of $C_4H_7^+$ ions

We generated the various $C_4H_7^+$ ions with varying internal energy by changing the number of stabilizing collisions with the bath gas, CS_2. We then used the spectral comparison method, described in the Experimental section, to compare the CAD spectra of the $C_4H_7^+$ ions generated from the same neutral precursor at differing energies (e.g. the $C_4H_7^+$ ions from cyclopropylcarbinyl chloride at low energy versus high energy). The divergence angle exceeds 6° for each species (Table 2). These results indicate that the $C_4H_7^+$ species generated from each of the isomeric precursors isomerize to a small extent which changes the composition of the ion mixture with increasing internal energy.

Two conclusions come from comparison of the CAD spectra from the $C_4H_7^+$ species generated from cyclopropylcarbinyl chloride with $C_4H_7^+$ from other sources (Table 2). First, the $C_4H_7^+$ derived from cyclobutyl chloride is significantly different from that generated from cyclopropylcarbinyl chloride. Second, based upon divergence angle, the $C_4H_7^+$ generated from cyclopropyl-

Table 2. Comparison of the CAD spectra of $C_4H_7^+$ ions generated from cyclopropylcarbinyl chloride with those from other sources

	Divergence angle, θ (°)[a]				
Precursor to $C_4H_7^+$	LH	LL′	LH′	HL′	HH′
Cyclopropylcarbinyl chloride	6.3				
Cyclobutyl chloride	6.8	19.4	21.0	20.4	20.5
4-chloro-1-butene (Homoallyl chloride)	6.1	8.8	4.2	3.7	4.9

[a] L′ and H′ represent the CAD spectra for the $C_4H_7^+$ ions generated from cyclopropylcarbinyl chloride at low energy and high energy, respectively. L and H represent the CAD spectra for the $C_4H_7^+$ ions generated from the specified neutral precursor at low energy and high energy, respectively. (see in Experimental section).

carbinyl chloride is most similar to that from homoallyl chloride. That each of the $C_4H_7^+$ ions originating from the three chloride precursors shows changes in the respective CAD spectra with increasing internal energy is not surprising in view of the many studies indicating that these species indeed are highly susceptible to rearrangement. These variations of CAD spectra with internal energy indicate that, during the short time after $C_4H_7^+$ ion generation afforded by our experiments, some isomerization of the initially formed ions occurred, at least for those ions formed with high internal energy. In addition, the $C_4H_7^+$ ions generated from the cyclopropylcarbinyl and homoallyl chlorides are similar, particularly at high internal energies, which is consistent with the theoretical prediction of Hehre and Hiberty[35] that the homoallyl cation would collapse to the cyclopropylcarbinyl cation, **3**, without activation.

The observation that the initial $C_4H_7^+$ ions generated from the cyclopropylcarbinyl and cyclobutyl chlorides are significantly different (Table 2; $\theta > 10°$) has structural and mechanistic implications. Majerski *et al.*,[5] based on labeling studies in solvolysis chemistry, proposed that the cyclopropylcarbinyl and cyclobutyl derivatives each solvolyze to initial ions that are similar in structure to the respective starting material. However, Schneider *et al.*[6] contend that the $C_4H_7^+$ ions from both precursors are the cyclopropylcarbinyl cation. The $C_4H_7^+$ ions generated in our study are formed in the solvent-free gas phase by the loss of chloride radical from the radical cations. Although our experimental conditions are different than those of solvolysis, the same question arises concerning the nature of the initially formed $C_4H_7^+$ ions from the cyclopropylcarbinyl and cyclobutyl precursors. Our results are consistent with those of Majerski *et al.*,[5] that is, the radical cations of cyclopropylcarbinyl chloride and cyclobutyl chloride, on loss of the chloride radical, generate respective ion populations that are significantly enriched in the carbenium ions, **3** or **4**, respectively.

Although the initial $C_4H_7^+$ ions or ion mixtures formed from the cyclopropylcarbinyl and cyclobutyl chlorides in the gas phase differ significantly, those same two precursors in superacid media generate essentially the same ion mixture. In superacid, both ions are long-lived, being produced and analyzed over a period of time ranging from milliseconds to tens of seconds. Hence ion formation, rearrangement and subsequent equilibration, which would entail carbon scrambling, occur over this time period. However, mass spectrometry samples ions within a much shorter time after generation (of the order of 10^{-6} s), before such processes have occurred, and in the complete absence of solvent.

In solvolysis experiments,[5] there is significantly reduced H–D label scrambling in ions originating from isotopically labeled cyclopropylcarbinyl substrates as compared with labeled cyclobutyl derivatives. On the time-scale of our experiments, we expect that H migration in ion **3** would be insignificant. For ion **4**, a 1,2-H shift from C-2 or C-4 to C-1 would be functionally equivalent to rotation by 90° about a perpendicular axis.

Evaluation of bimolecular adduct ion mixtures generated from $C_4H_7^+$ ion–neutral reactions

We conducted two series of bimolecular gas-phase reactions (see Experimental section), using methanol and ethene as neutral reagents in separate experiments, to gain further insight into the $C_4H_7^+$ species initially produced from cyclopropylcarbinyl and cyclobutyl substrates. We chose methanol as a reagent because it is a good gas-phase nucleophile and, in fact, it reacts readily with the $C_4H_7^+$ ions to produce adduct ions. Furthermore, we expected that methanol, which possesses a heteroatom, would produce adduct ions that would dissociate via heteroatom-driven, structure-specific pathways and hence would provide insight into the skeletal structure of the reactant $C_4H_7^+$ ions. We chose ethene as a potential selective reagent on the basis of Cramer and Barrows' computational work.[25] The bimolecular reactions conducted are shown in Eqns (7)–(10).

$$\text{MeOH} + C_4H_7^+ \text{ from cyclopropylcarbinyl chloride} \longrightarrow \text{adduct(s)} \quad (7)$$

$$\text{MeOH} + C_4H_7^+ \text{ from cyclobutyl chloride} \longrightarrow \text{adduct(s)} \quad (8)$$

$$\text{ethene} + C_4H_7^+ \text{ from cyclopropylcarbinyl chloride} \longrightarrow \text{adduct(s)} \quad (9)$$

$$\text{ethene} + C_4H_7^+ \text{ from cyclobutyl chloride} \longrightarrow \text{adduct(s)} \quad (10)$$

The $C_4H_7^+$ ions derived from cyclopropylcarbinyl and cyclobutyl chlorides generate $C_5H_{11}O^+$ adduct ions at *m/z* 87 [Eqns (7) and (8)]. On the basis of the conclusions of Majerski *et al.*[5] and Schneider *et al.*,[6] we expect that the $C_4H_7^+$ reactant, generated from the cyclopropylcarbinyl precursor and involved in reaction with methanol, is principally **3**. In the previous section, we presented evidence that the $C_4H_7^+$ generated from the cyclobutyl precursor cannot be predominantly **3**. Instead, **4** likely represents a significant, if not exclusive, species in the $C_4H_7^+$ ion population derived from cyclobutyl chloride.

The structures of the $C_5H_{11}O^+$ adduct ions, as reflected in their CAD spectra, are significantly different, as established by a divergence angle of 11.0° (derived from data in Table 1). The difference is consistent with expectations that **3** is the reactant in reaction (7) and **4** is the major reactant in reaction (8). The difference may mask the lesser presence of **3** in the composition of the $C_4H_7^+$ derived from cyclobutyl chloride.

The specific dissociations of the $C_4H_7^+$–methanol

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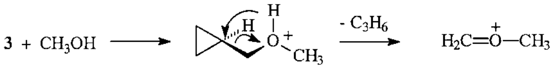
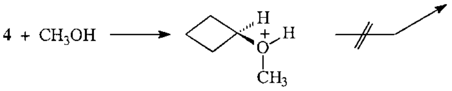
adducts provide evidence regarding the nature of **3** and **4** and of their reactions with methanol. The predominant fragment ion (≈40% total ion current) generated upon dissociation of the adduct formed in reaction (7) is a $C_2H_5O^+$ ion of *m/z* 45. This ion can reasonably be derived from an adduct whose carbon skeleton resembles that of cyclopropylcarbinyl. However, an adduct that contains an intact cyclobutyl moiety is not expected to undergo fragmentation readily to yield a $C_2H_5O^+$ ion of *m/z* 45 [compare Eqns (11) and (12)].

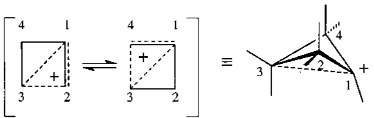


(11)



(12)

The $C_2H_5O^+$ ion of *m/z* 45 is also the predominant fragment ion (≈34% total ion current, a reproducible difference from that of reaction with **3**) generated from the methanol adduct formed in reaction (8). If the cyclobutyl precursor generates initially only **4**, then **4** must react with methanol to produce an adduct ion possessing a cyclopropylcarbinyl moiety. This common reactivity implies that **3** and **4** share a common reactive outlet. Roberts and co-workers[10–13] proposed that the bicyclobutonium ion, **4**, was initially formed from cyclobutyl precursors but that the cyclopropylcarbinyl and cyclobutyl products were produced during solvolysis by nucleophilic attack at carbons C-2 (C-4) or C-1, respectively, of **4**.



4

(13)

Nucleophilic attack by methanol at C-2 or C-4 of **4** is a reactive outlet that is the functional equivalent of nucleophilic attack at the exocyclic carbon of **3**, and explains the shared reactivity between **3** and **4**. In contrast, methanol attack at C-1 generates an adduct ion not produced in the reaction between methanol and **3**. (Nucleophilic attack at C-3 would not product a viable adduct.) Thus, methanol attack at various sites of **4** gives different product(s) than attack on **3**, which can undergo methanol attack only at the exocyclic carbon, thus explaining why the adduct ions produced in reactions (7) and (8) are not identical. Nevertheless, both produce a fragment ion of *m/z* 45 upon collisional activation.

If, instead, the cyclobutyl precursor generates either initially or within the time frame of these experiments (of the order of 10^{-6} s) a $C_4H_7^+$ ion mixture consisting of both **3** and **4**, considerations in addition to those of the preceding discussion must be made. The components of such a mixture would then react with methanol as outlined in both reactions (7) and (8). As discussed earlier, **3** would react with methanol to produce an adduct ion that has a cyclopropylcarbinyl moiety and would decompose upon collisional activation to yield the $C_2H_5O^+$ fragment ion at *m/z* 45 [reaction (11)]. The differences observed in the CAD spectra of the adducts formed from $C_4H_7^+$ ions from cyclopropylcarbinyl and cyclobutyl substrates suggest that **4** must possess reactive outlet(s) not available to **3**, the most reasonable being methanol attack at C-1. The question then is whether **4** *necessarily* possesses a reactive outlet that is common with **3**. We note that the CAD spectra of the adduct ions generated in reactions (7) and (8), while different from one another, are *more* similar to one another than are the CAD spectra of the reactant $C_4H_7^+$ ions (divergence angle, θ, of 11° for the adducts vs θ >19° for the reactant $C_4H_7^+$ ions in Table 2). This observation implies that **3** and **4** possess a common reactive outlet, presumably methanol attack at C-2 or C-4 of **4**, which is functionally equivalent to methanol attack directly upon **3**.

Table 3. Comparison of the CAD spectra of the $C_6H_{11}^+$ adduct ions formed in the bimolecular reaction of the $C_4H_7^+$ from cyclopropylcarbinyl chloride with ethylene and the $C_6H_{11}^+$ ions from other sources

	Divergence angle, θ (°)[a]				
Precursor to $C_6H_{11}^+$ ions	LH	LL′	LH′	HL′	HH′
$C_4H_7^+$ (cyclopropylcarbinyl chloride) + ethene	1.3				
$C_4H_7^+$ (cyclobutyl chloride) + ethene	8.1	4.1	4.8	11.3	11.8
Cyclohexyl chloride	7.9	12.5	11.7	18.6	17.9
Cyclopentylcarbinyl chloride	9.6	9.6	9.7	4.8	4.8
3-Chloro-1-hexene (*n*-propylallyl chloride)	3.3	11.2	11.6	8.5	8.9
6-Chloro-1-hexene	2.4	7.1	7.6	5.7	6.4
1-Chloro-1-methylcyclopentane	1.6	8.8	8.6	9.9	9.6

[a] L′ and H′ represent the CAD spectra for the $C_6H_{11}^+$ adduct ion generated in the reaction of the $C_4H_7^+$ ions from cyclopropylcarbinyl chloride with ethylene at low energy and high energy, respectively. L and H represent the CAD spectra for the other $C_6H_{11}^+$ ions generated from the specified precursor at low energy and high energy, respectively (see in Experimental section).

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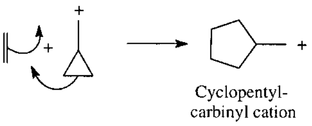
Evaluation of $C_4H_7^+$ ion–ethene bimolecular adducts

Based on the theoretical work of Cramer and Barrows,[25] we expect ethene to undergo a cycloaddition with **3** to give the cyclopentylcarbinyl cation [Eqn. (14)], but not to react with **4**.



(14)

The $C_4H_7^+$ species from cyclopropylcarbinyl chloride does react with ethene to product a $C_6H_{11}^+$ adduct [reaction (9)]. The CAD spectra of the $C_6H_{11}^+$ adduct does not change appreciably with internal energy ($\theta = 1.3°$, Table 3). This result indicates that the adduct ion is stable and its bonding is covalent. If the adduct had an appreciable population of ion–dipole complex (a $C_4H_7^+$–ethene complex), the amount of *m/z* 55 ion produced upon collision activation would exhibit significant changes with ion internal energy, because the stability of an ion–dipole complex is sensitive to its internal energy.

Model $C_6H_{11}^+$ cations were generated, and their CAD spectra as a function of internal energy were collected for the purpose of comparison. The specific model compounds chosen for generation of the $C_6H_{11}^+$ species were cyclohexyl, cyclopentylcarbinyl, *n*-propylallyl, 5-hexenyl and 1-methylcyclopentyl chlorides. These ions are generated via a unimolecular decomposition of the precursor radical cations, and are expected to be covalent species. Hence, direct comparison of CAD spectra with that of the adduct of reaction (9) should be justified. The predominant fragmentation channel of all $C_6H_{11}^+$ ions is the loss of neutral ethene to give an *m/z* 55 ion. Among the CAD spectra of the model cations, that of the cyclopentylcarbinyl cation compares most favorably with the CAD spectra generated from the adduct ion [reaction (9)]. As the internal energy of the model cyclopentylcarbinyl cation is increased, its CAD spectra converge to that of the adduct with a divergence angle of $<5°$ (Table 3). This result is consistent with Cramer and Barrows' prediction that the cycloadduct formed from **3** and ethene is the cyclopentylcarbinyl cation.

Ethene also reacts with the $C_4H_7^+$ from cyclobutyl chloride [reaction (10)], forming an adduct. The CAD spectra of the adduct change with internal energy ($\theta = 8.1$, Table 3), unlike the CAD spectra of the previous adduct which is nearly invariant. For the adduct in reaction (10), the major contributor to spectral change is the fragmentation to the *m/z* 55 ion, the relative yield of which increases by ≈ 30 % with increasing internal energy. The yields of the *m/z* 55 ions from the model ions, on the other hand, decrease with increasing internal energy. The fragmentation of the adduct formed in reaction (10), therefore, must occur via some exit channel not accessible to the other adduct or the model ions.

Comparison of the CAD spectra of the adduct formed in reaction (9) under both low and high internal energy conditions with those of the adduct formed in reaction (10) under low internal energy conditions yields a divergence angle in both cases of $<5°$, thus implying a common structure within the products. However, the CAD spectra of the adduct generated with high internal energy in reaction (10) do not match any of those of the adduct formed in reaction (9). Furthermore, the CAD spectra of the adduct formed in reaction (10) do not match those of the cyclopentylcarbinyl cation ($\theta > 5.0$ for all internal energy conditions, data not shown). Thus, reaction (10) must generate an adduct that is either different from that formed in reaction (9) or a mixture in which the product of reaction (9) is a minor component. The differences in the CAD spectra of the adducts must be attributable to **4** reacting differently with ethene than does **3**. For the purposes of this investigation, we are interested in whether **4** reacts with ethene to produce a cycloaddition product, the cyclopentylcarbinyl cation, as does **3**. It does not, verifying the theoretical predictions of Cramer and Barrows.[25]

CONCLUSION

The $C_4H_7^+$ population formed initially from cyclobutyl chloride in the dilute gas phase is not exclusively, or even predominantly, cyclopropylcarbinyl cation **3**. A significant contribution from the bicyclobutonium ion **4** is indicated based on differences in reactivity with the nucleophile, methanol. The bicyclobutonium ion **4** must have reactive outlet(s) with methanol not available to the cyclopropylcarbinyl cation **3**. Nucleophilic attack at C-2 or C-4 is the functional equivalent of nucleophilic attack at the exocyclic carbon of the cyclopropylcarbinyl cation, whereas nucleophilic attack at C-1 yields products that cannot be generated by nucleophilic attack on **3**. These experimental observations are in agreement with the predicted reactivity of the bicyclobutonium ion as originally postulated by Roberts and co-workers.[10–13] Furthermore, the cyclopropylcarbinyl cation reacts with ethene to generate the cyclopentylcarbinyl cation, whereas the bicyclobutonium ion, although reactive with ethene, does not generate any significant amount of cyclopentylcarbinyl cation. These observations are in accord with the theoretical predictions of Cramer and Barrows,[25] and also provide experimental evidence that the cyclopentylcarbinyl cation does react differently than the bicyclobutonium ion.

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