

# Atmospheric Pressure Chemical Ionization of Alkanes, Alkenes, and Cycloalkanes

Suzanne Ehart Bell, Robert G. Ewing, and Gary A. Eiceman

Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, New Mexico, USA

Zeev Karpas

Nuclear Research Center, Negev, Beer-Sheva, Israel

Normal and cyclic alkanes and alkenes form stable gas-phase ions in air at atmospheric pressure from 40 to 200 °C when moisture is below 1 ppm. Ionization of alkanes in a  $^{63}\text{Ni}$  source favored charge transfer over proton transfer through pathways involving  $[M - 1]^+$  and  $[M - 3]^+$  ions. Ion mobility spectra for alkanes showed sharp and symmetrical profiles while spectra for alkenes suggested fragmentation. Ion identifications were made by using mass spectrometry, and ionization pathways were supported by using deuterated analogs of alkanes and alkenes. Alkanes were ionized seemingly through a hydrogen abstraction pathway and did not proceed through an alkene intermediate. New methods for interpretation of mobility spectra utilizing ion mobility spectrometry, atmospheric pressure chemical ionization mass spectrometry, chemical ionization mass spectrometry, and ion mobility spectrometry-mass spectrometry data were demonstrated. (*J Am Soc Mass Spectrom* 1994, 5, 177-185)

Interest in ion mobility spectrometry (IMS) as a field monitor has arisen from technical considerations of size, weight, and power. However, IMS detection of alkanes and aromatics, compounds of significant concern in environmental and industrial settings, has been limited by poor sensitivities, typically parts-per-million in air. This problem may be attributed to difficulties in chemical ionization (CI) of hydrocarbons rather than to ion mobility characterization.

Until recently, the low proton affinities of alkanes were considered responsible for poor response in IMS [1], suggesting comparatively inefficient proton transfers from IMS reactant ions such as  $(\text{H}_2\text{O})_n\text{H}^+$  ( $n = 2$  to 4). Trace detection limits and high quality mobility spectra have been obtained for alkanes when the values for  $n$  in  $(\text{H}_2\text{O})_n\text{H}^+$  have been reduced to  $\approx 1$  with low moisture in helium [2] and high temperatures in air [3].

Karasek et al. [4] first examined the response of alkyl ions in IMS by using various  $n$ -alkyl halides in 1973. Alkyl halides undergo dissociative electron capture in the negative mode and ion pair formation, with positive mode ions presumably created from the alkyl backbone. Positive ions for alkyl halides were observed, and resulting spectra exhibited multiple peaks. The most abundant ion was postulated to be  $[M - 1]^+$  through a correlation between reduced mobility and

formula weight. Operating temperature of the IMS was 135 °C and moisture levels were not reported. Later, a series of  $n$ -alkanes ( $\text{C}_5\text{H}_{12}$  to  $\text{C}_{15}\text{H}_{32}$ ) was characterized by IMS and compared to CI mass spectrometry (CIMS) [5]. Several routes for ion formation were proposed and the apparent dominant route favored  $[M + 1]^+$ . A linear relationship existed between the molecular weight and reduced mobility of the alkanes from hexane to dodecane and the spectra showed evidence of fragmentation. The ionization of these alkanes occurred in nitrogen at a temperature of 135 °C and with approximately 10 ppm moisture.

Recently, IMS response to small alkanes at 200 °C in dry helium was reported [2]. Alkane response in IMS was governed by two distinct processes in the dry helium system. Low moisture levels prolonged lifetimes of high energy intermediate ions, and water cluster formation was no longer the dominant ionization pathway. Rather, at moisture levels of 1 to 10 ppb, charge transfer reactions from a metastable helium ion appeared to control ionization. These results posed questions about the ionization reactions occurring. Was helium the sole agent for charge transfer and if not, could these same charge transfer reactions occur in dry nitrogen?

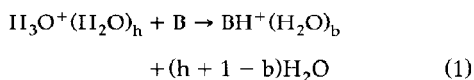
Atmospheric pressure chemical ionization mass spectrometry (APCI-MS) using  $^{63}\text{Ni}$  sources and CIMS have been used as reference to the reactions inside an ion mobility spectrometer. However, findings from these instruments, especially CIMS, cannot be directly utilized because of differences in pressures, reagent

Address reprint requests to Dr. S. E. Bell, Department of Chemistry and Biochemistry, New Mexico State University, P.O. Box 30001—Department 3C, Las Cruces, NM 88003-0001.

gases, temperature, and moisture levels. Still, similarities in formation of gas-phase ions in IMS and these techniques combined with the availability of commercial instrumentation have been factors in comparisons. Few laboratories have access to ion mobility spectrometry-mass spectrometry (IMS-MS) instruments.

Keough [6] used dimethylether as a reagent gas with alkanes and found primarily  $[M - 1]^+$  and  $C_nH_{2n+1}^+$  fragments. Spectra of branched alkanes showed bond cleavages occurring at branching points, with patterns that were highly dependent on structure. Other ionization processes included cleavages, ring breakage or contraction, and rearrangements. Comparable results were obtained for deuterated decane by using methane as a reagent gas [7]. The major ion was  $[M - 1]^+$  and significant quantities of alkyl and alkenyl fragments were observed. Ions were formed through internal rearrangements of the  $[M - 1]^+$  species via hydride shifts and through loss of olefin moieties to fragment alkyl ions. Finally, nitric oxide reagent gas led to formation of  $[M - 1]^+$  and  $[M - 3]^+$  in *n*-alkanes and fragmentation in branched species [8]. Hydride elimination was found to favor hydrogens in carboniums in the order  $3^\circ > 2^\circ > 1^\circ$ .

Although alkanes have not been the subject of dedicated APCI-MS work, certain studies provide details necessary to postulate ion formation mechanisms. In 1988, the role of moisture in APCI-MS was examined by Sunner et al. [9, 10], who assumed the main reactant ions in the APCI-MS were hydronium ion clusters and that the primary route of formation of product ions is through proton transfer per eq 1. More specifically, the reaction of interest is



Sensitivity of the APCI-MS to the analyte B was determined by gas-phase basicity and by the corresponding gas-phase acidity of the clustered proton. The proton acidity was a function of the number of water molecules in the reactant ion cluster. Moreover, analytes could be classified into three groups. The first consisted of compounds for which the APCI-MS was extremely sensitive. These compounds possessed high gas-phase basicities and were designated as "K" compounds because their reactions (eq 1) were kinetically controlled. At the opposite extreme were the compounds with low basicities, as low or lower than water, designated as "L" compounds. Such compounds respond poorly, if at all, under APCI-MS conditions. The third group of compounds consisted of those with intermediate gas-phase basicities and were designated as "T" for reactions that fall under thermodynamic control. In such cases eq 1 becomes a dynamic equilibrium. The alkanes and alkenes would be classified as T or L compounds, depending on the compound selected.

For L compounds, the hydrates of  $BH^+$  are relatively unstable. Additionally, high moisture levels typical for APCI-MS and IMS tend to force the equilibrium in reaction 1 toward the reactants. These factors result in the low sensitivity toward the L compounds and by implication, low sensitivities to alkanes. Sunner et al. [9, 10] showed increased temperatures of the ionization source dramatically increased sensitivity toward the L compounds. This increase was attributed to progressive dehydration of the proton clusters at higher temperatures. Similar dehydration of reactant ions in IMS has been previously demonstrated [3, 11].

Alkanes have significance for industrial and environmental monitoring and as probes for APCI-MS ionization processes. Possessing neither heteroatoms nor permanent dipole moments, alkane interactions in the instrument present less formidable interpretive challenges than molecules such as alcohols and amines. The presence or absence of a permanent dipole will influence the initial attraction and subsequent interaction of the neutral and charged reactant ion. More important, charge delocalization can influence mobility by dictating interactions between the drift gas and the ion-molecule complexes [12, 13]. Using the alkanes to probe ion-molecule chemistry can simplify interpretation of the roles individual chemical properties play in determining mobility.

The investigation has two objectives: (1) to perform an extensive study of IMS response to alkanes at different temperatures under controlled moisture conditions, and (2) to identify routes of ion formation. Findings were examined to identify trends in ion mobility and to deduce what factors were important in determination of those trends. Also, alkanes were studied by using APCI-MS and results were related to mobility spectra, selectivity, and sensitivity.

## Experimental

### Instrumentation

Two ion mobility spectrometers were used for data collection, each equipped with a gas chromatograph (GC) for sample introduction. Operating parameters for these instruments are summarized in Table 1. The Volatile Organic Analyzer, or VOA (Graseby Ionics, Ltd., Watford, Herts, UK), was used to collect spectra at 200 °C. The drift gas (air) was extensively purified and dried by using a series of redundant in-line filters for hydrocarbons,  $O_2$  (for  $N_2$  carrier gas), and water. The last filter in the gas line was a high capacity indicating moisture trap (R & D Separations, Rancho Cordova, CA). This trap was carefully monitored, and no indications of moisture breakthrough were observed throughout the experiments. Instruments were not available to measure moisture levels precisely, but based upon the soundness of the gas manifold and filter system, and the moisture level rating of the trap effluent (30 ppb, personal communication, Technical

Table 1. VOA GC/IMS parameters

Gas Chromatograph	EVM	VOA
Carrier gas:	Air <sup>a</sup>	Nitrogen
Flow rate:	Set internally	0.9 mL/min
Temperature program:	80° (isothermal)	80°–180 °C, 8.0°/min
Column	BP-1, 10 meter	Quadrex (New Haven, CT) 30m × 0.25 mm × 0.25 μm DB-5 equivalent Splitless
Injector	NA	
Flows		
Drift gas:	Air	Air
Sheath flow:	NA	60 mL/min
Cell flow:	Set internally	300 mL/min
Acquisition		
Waveforms averaged:	8	4
Number of samples:	512	640
Frequency (kHz):	40	40
Waveforms:	1	1
Shutter Pulse		
Frequency (Hz):	40	40
Delay (us):	1000	0
Width (us):	180	200
Source:	External	Internal

<sup>a</sup> Both the carrier gas and drift gases are obtained from air drawn into the EVM via a pumping system. An internal molecular sieve/charcoal pack is used to clean and dry the recirculating drift and carrier gases.

Service Department, R & D Separations), moisture in the VOA was reasonably assumed to be less than 1 ppm. Carrier gas for the GCs was similarly scrubbed and dried.

Mobility spectra were also collected at 40 °C by using an Environmental Vapour Monitor (EVM, Graseby) which has been described elsewhere [14]. A recirculating supply of drift and carrier gases was passed through molecular sieve and charcoal filters. Exact moisture levels in the EVM were undetermined, but comparatively dry conditions (1 ppm or better) were suggested from the reduced mobility of the reactant ion peak.

Spectra from both systems were collected on an IBM-compatible personal computer using digital signal averaging boards and Advanced Signal Processor (ASP, Graseby) software. The ASP software was used to control spectral acquisition, display, storage, and instrument operation.

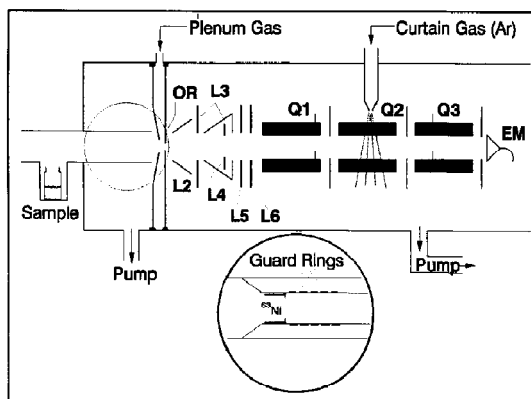
Ionization studies were conducted by using an atmospheric pressure chemical ionization/mass spectrometer, the TAGA-6000 tandem mass spectrometer (Sciex, Toronto, Canada). The TAGA was equipped with a <sup>63</sup>Ni ionization source identical to that used in the mobility spectrometers. Details of operational conditions are given elsewhere [15–17]. A schematic of the TAGA and APCI inlet is shown in Figure 1.

### Chemicals and Procedures

Hydrocarbon standards were purchased from Aldrich Chemical Co. (Milwaukee, WI) and ChemService (West Chester, PA) at highest available purity. Samples were

introduced into the VOA through two methods. The most volatile hydrocarbons were introduced directly into the ionization region of the IMS via head space injection. All other compounds were introduced via the GC. Samples for EVM analysis were diluted in methylene chloride and introduced through a heated port located near the EVM inlet. One-microliter samples were injected into the inlet and the vapors passed into the EVM via a continuous flow of nitrogen.

A chemical standard, 2,4-lutidine, was analyzed



**Figure 1.** TAGA and sample introduction system. The sample liquid is placed in a vial and secured as shown. A flow of clean, dry air nitrogen flows over the sample and carries vapors into the ionization chamber. A <sup>63</sup>Ni foil at the end of the glass tube provides beta particles for the ionization and ions are drawn into the TAGA where they are focused and directed into the quadrupoles.

daily on the VOA and EVM and was used for a normalization standard. This procedure was used for two reasons. Calculation of a reduced mobility value requires a knowledge of the electrical field strength within the drift region of the mobility spectrometer [1], which was unavailable for both the VOA and EVM. Additionally, reduced mobilities are dependent upon temperature and pressure, and use of the lutidine standard compensates for those dependencies [18]. The reduced mobility of lutidine was taken to be  $1.95 \text{ cm}^2/(\text{V s})$  at all temperatures [18].

## Results and Discussion

### Mobility and Structure

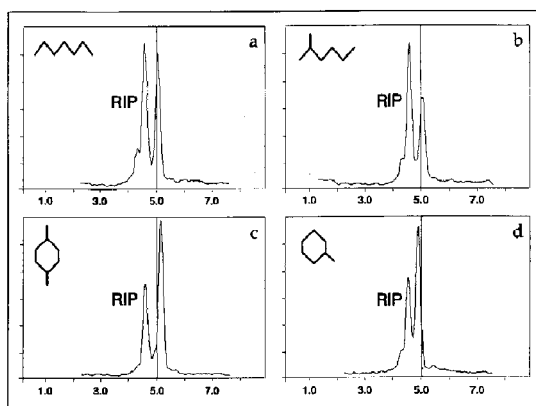
Example mobility spectra in air are presented in Figure 2. These spectra were acquired on the EVM operating at  $40^\circ\text{C}$  and are typical of alkane spectra obtained at  $40^\circ\text{C}$  and  $200^\circ\text{C}$ . The spectra were similar in appearance to the low moisture spectra reported by Kojiro et al. [2] and showed none of the fragmentation reported by Karasek et al. [5]. Indeed, alkane spectra here showed greater similarity to alkane spectra obtained in dry helium than to spectra obtained in moist nitrogen. Identification of ionization routes responsible for these spectra and the relationship to pathways proposed by Kojiro et al. could not be elucidated without APCI-MS.

Prior to APCI-MS characterization of the alkanes, a plot of inverse reduced mobility as a function of formula weight was prepared. Inverse reduced mobilities were used to preserve the intuitive relationship between drift time and size-to-charge ratio. This plot would reveal if expected relationships between mobility and molecular weight (i.e., increasing molecular weight corresponding to longer drift times, lower mo-

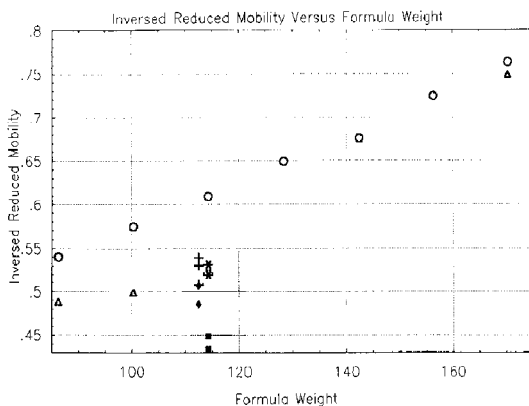
bility, and larger inverse mobility) were obeyed. Deviations from the expected patterns would indicate either instrument or procedural errors or unexpected differences in ion-molecule chemistry occurring in the instrument. Neither problem was observed.

A composite plot of inverse reduced mobility of selected alkanes versus formula weight is shown in Figure 3. Results from  $40^\circ\text{C}$  and  $200^\circ\text{C}$  are shown and a linear relationship was observed for the n-alkanes at  $200^\circ\text{C}$  and a nearly linear relationship was observed at  $40^\circ\text{C}$ . A similar relationship (not shown) among cycloalkanes from cyclopentane to cyclodecane was observed. Increased mobilities at  $200^\circ\text{C}$  relative to those at  $40^\circ\text{C}$  are due to dehydration of the product ion [3, 11]. Results for the branched hexanes and disubstituted cyclohexanes were obtained from octane isomers and two branched heptanes. The compactness of the branched and disubstituted compounds relative to n-alkanes was evident in reduced mobilities that were bracketed by mobilities of n-hexane and n-heptane. Identical molecular weights (branched hexanes 114, disubstituted cyclohexanes 112) nullified the effects of molecular weight on mobility. Differences in reduced mobilities and spectral patterns within the subclasses may be attributed to structural differences and not to molecular weight differences.

Structure will also determine how temperature and hydration influence mobility. The difference in mobilities between disubstituted cyclohexanes at  $40^\circ\text{C}$  and  $200^\circ\text{C}$  is smaller than the corresponding difference in either straight chain or branched hydrocarbons. This implies the extent of hydration of disubstituted cyclohexanes is less than that of the other alkanes studied. If hydration sphere size is little different between  $40^\circ\text{C}$



**Figure 2.** Example mobility spectra. (a) n-Heptane, (b) 2-methyl hexane, (c) 1,4-dimethylcyclohexane, (d) methyl cyclohexane. The x-axis units are milliseconds and the y-axis units are millivolts. The reactant ion peak and molecular structures are shown for each compound, and a line is drawn at 5.0 ms for reference. All spectra were collected at  $40^\circ\text{C}$  using the EVM at an estimated water concentration of 1 ppm.



**Figure 3.** Inversed reduced mobility versus formula weight. Shown are inverse reduced mobilities of n-alkanes of pentane through dodecane (circle:  $200^\circ\text{C}$ ; triangle,  $40^\circ\text{C}$ ), branched alkanes (asterisk:  $200^\circ\text{C}$ ; square,  $40^\circ\text{C}$ ), and disubstituted dimethyl cyclohexanes (plus:  $200^\circ\text{C}$ ; diamond,  $40^\circ\text{C}$ ). The branched alkanes included 2- and 4-methyl hexane and 2,5-dimethyl hexane. The disubstituted methyl cyclohexanes included 1,1-, *c*-1,2-, and 1,4-dimethyl cyclohexane. Labels omitted for clarity. The x-axis is in amu and the y-axis in  $(\text{V S})/\text{cm}^2 (1/K_0)$ .

and 200 °C, increasing the temperature of the IMS will not significantly alter mobility. The pattern observed within the disubstituted cyclohexanes is likely a steric effect. A similar plot of cycloalkanes (not shown) showed differences in mobilities between the two temperatures of the same magnitude seen with n-alkanes. Adding substituents to the ring limits the number of accessible and stable protonation/hydration points available on the molecule. As a consequence, few water molecules associate with the ion regardless of temperature.

Charge delocalization was also important in controlling hydration influences on mobility. The attraction of an ion to water decreases as charge delocalization increases. The cyclic molecules delocalize charge more efficiently than their branched counterparts and thus should hydrate to a lesser degree. The observable outcome was the same as the steric effects discussed above, a smaller stable hydration sphere and smaller relative changes in mobility between 40 °C and 200 °C.

The lowest mobilities observed were for the branched alkanes at 40 °C. Branched alkanes, particularly 2-methyl hexane, are prone to "wobble" at reduced temperatures as recognized for amines, where molecules become unbalanced following asymmetric protonation and hydration [12, 13]. Hydration should accentuate wobbling, but dehydration should mute the effect. This pattern may be observed in Figure 3, where mobilities of dehydrated branched species approach those of the dehydrated substituted cyclohexanes while the corresponding hydrated mobilities show greater differences between the two temperatures.

### APCI-MS of Alkanes

Representative alkanes were characterized by using APCI-MS and the results are shown in Table 2. The results include fragment ions,  $[M - 1]^+$ , and  $[M - 3]^+$  ions as composites of protonated and monohydrated species. Of particular interest was the predominance of  $[M - 3]^+$  and  $[M - 3]^+ \text{H}_2\text{O}$  to the extent that in several cases, these ions were seen in greater abundances than the  $[M - 1]^+$  species. Pathways for  $[M - 1]^+$  have been previously described in IMS [4, 5], and fragmentation has been reported [19]; however, ionization to  $[M - 3]^+$  has never been seen in IMS or IMS-MS. Identification of  $[M - 3]^+$  ions was unexpected and previously unreported in the APCI-MS of alkanes; however,  $[M - 3]^+$  species were seen in CIMS studies of alkanes [7, 8]. Because the appearance of  $[M - 3]^+$  ions was unexpected here and the ions were so pervasive, two additional experiments were undertaken to confirm reliability of the identifications.

Perdeuterated hexane, cyclohexane, and methyl cyclohexane were characterized by using the same APCI-MS conditions employed to generate the data in Table 2. The results for the deuterated compounds paralleled those obtained for the nondeuterated equivalents. Deuterated hexane produced primarily  $[M - 2]^+$ , while the deuterated cyclic species produced primarily  $[M - 6]^+$  ions and fragments. These findings confirm that  $[M - 1]^+$  and  $[M - 3]^+$  ions initially observed were genuine and not caused by procedural errors or contamination.

A portion of the  $[M - 3]^+$  species reported in Table

Table 2. Summary of APCI data

Category	Compound	MW	$K_0^a$	M - 1	M - 3	F <sup>b</sup>
Straight-chain	Hexane	86	1.85	Y	Y	Y
	Heptane	100	1.74	Y	Y	Y
	Octane	114	1.64	Y	Y	Y
	Nonane	128	1.54	Y	N	Y
	Dodecane	170	1.31	Y	N	N
Branched	2-methyl hexane	100		N	Y	Y <sup>c</sup>
	2,2,4-trimethyl pentane			N	N	Y <sup>c</sup>
Cyclics	Cyclohexane	84	2.10	Y	Y	Y
	Cycloheptane	98	1.98	Y	Y	Y
Single Substituted Cyclics	Methyl cyclohexane	98	1.97	Y	Y	N
	Ethyl cyclohexane	112	1.87	N	Y	N
	Isopropyl cyclohexane	126	1.76	Y	Y	N
	1,1-dimethyl cyclohexane	112	1.97	N	Y	Y
	c-1,2-dimethyl cyclohexane	112	1.89	N	Y	N
Disubstituted Cyclics	1,4-dimethyl cyclohexane	112	1.86	Y	Y	Y

<sup>a</sup> Reduced mobility at 200 °C, normalized to 2,4-lutidine.

<sup>b</sup> Apparent fragment ions, excluding water clusters: 55, 73, 91, 109, 127, 145 and 163.

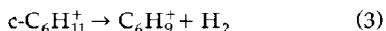
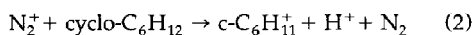
<sup>c</sup> Major peak was a fragment peak. Refer to text for discussion.

2 was detected as a monohydrated species  $[M + 15]^+$ . Verification of  $[M + 15]^+$  as hydrated  $[M - 3]^+$  was deemed critical and accomplished using collision-induced dissociation (CID) of cyclohexane. The  $m/z$  99 ion of the cyclohexane ( $[M + 15]^+$ ) was isolated as the parent ion and subjected to CID using argon in the collision chamber. A small daughter ion peak was recorded at  $m/z$  81, corresponding to the  $[M - 3]^+$  ion, assuming the loss of water. Ion intensity at  $m/z$  18 ( $H_2O$ ) was also observed. A similar water loss was identified from hydrated clusters of the  $[M - 1]^+$ . These results combined with findings from APCI-MS of deuterated species provided confidence in the authenticity of the  $[M - 1]^+$  and  $[M - 3]^+$  ions.

Identification of an  $[M - 3]^+$  ion suggested that under dry conditions, alkanes may ionize through alkene intermediates. Alkenes have higher proton affinities than corresponding alkanes (e.g., cyclohexane pA: 189 kcal/mol versus cyclohexene: 212 kcal/mol [20]) and can be detected readily in IMS. Because  $[M - 3]^+$  ions have never been reported in APCI-MS or IMS-MS, precedents in CIMS were sought.

Hunt and Harvey [8] detected  $[M - 3]^+$  using NO as the reagent gas, and rationalized the ion through a long-lived collisional complex consisting of the alkane,  $NO^+$ , and neutral NO. However, this pathway or similar pathways using  $N_2^+$  as the hydride extractor are not applicable to APCI-MS, principally due to the role played by nitrogen in the two systems. The CIMS work was conducted at 1 torr at undisclosed or undetermined moisture levels. Effects of nitrogen were minimized in the system because large amounts tended to suppress formation of  $[M - 3]^+$ . Conversely, in the TAGA and mobility spectrometers, air and nitrogen were used extensively as drift and carrier gases, and NO, if present, was at low levels. Background levels of NO were not seen in the APCI-MS and no evidence of a NO reactant ion was observed in any of the mobility spectra. Finally, no  $[M - 3]^+$  was recorded in alkanes larger than hexane, but was widespread in the APCI-MS results shown in Table 2. Therefore, the mechanism of formation of the  $[M - 3]^+$  in the APCI-MS must be different than that in NO-CIMS.

Elimination reactions to  $[M - 3]^+$  are common under electron impact mass spectrometry, but have not been invoked for CIMS because the activation energy for such unimolecular decompositions is +46 kcal/mol [6]. However, a stepwise reaction involving formation of  $[M - 1]^+$  followed by elimination of  $H_2$  is energetically feasible under APCI-MS conditions. Equations 2 and 3 illustrate, using cyclohexane as an example.



The dissociative charge transfer reaction 2 is endothermic,  $\Delta H = 16.3$  kcal/mol, while the subsequent dehydrogenation is exothermic ( $-16.0$  kcal/mol), pro-

ducing an overall thermoneutral reaction. A portion of the  $[M - 1]^+$  ions will be hydrated and detected as the charged, hydrated species. However, some  $[M - 1]^+$  ions would be available as the starting point for reaction 3. The initial collision between the cyclohexane and nitrogen can provide the energy required for charge transfer, while the second stage of the reaction is thermodynamically favored. Formation of  $[M - 1]^+$  ions via charge transfer has been previously reported in CIMS, APCI-MS and IMS-MS, supporting the reaction in eq 2. Moreover, the reaction in eq 3 is exothermic, so the  $H_2$  elimination likely proceeds as written. The extent of reaction 3 under APCI-MS conditions could not be determined. In addition, reaction 3 could produce two hydrogen atoms instead of hydrogen gas. Such a reaction is highly endothermic and would not occur spontaneously. If  $H_2$  elimination occurs, it does so as per eq 3.

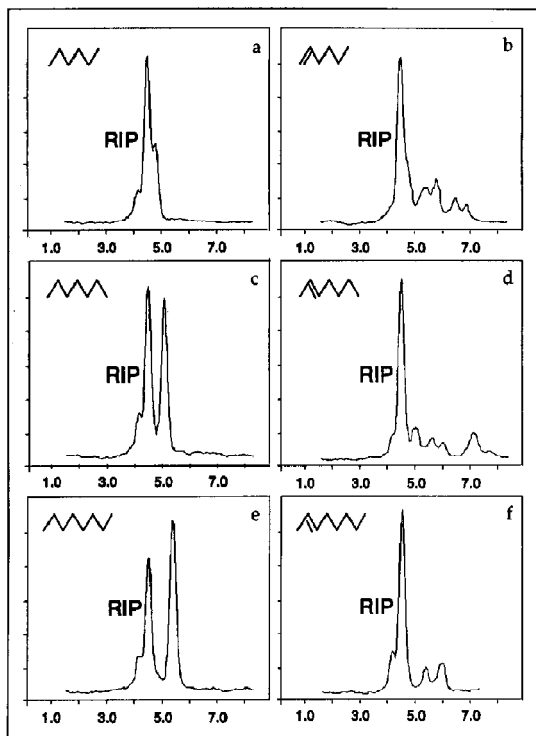
### IMS of Alkane / Alkene Pairs

$[M - 3]^+$  ion suggests ionization of alkenes as part of a stepwise reaction  $M \rightarrow [M - 1]^+ \rightarrow H_2$  elimination  $\rightarrow$  alkene. If genuine, this pathway should be evident in spectral features of APCI-MS and IMS. Selected alkane/alkene pairs were characterized, and representative spectra are shown in Figure 4. The alkene mobility spectra showed multiple broad peaks and baseline elevation characteristic of fragmentation reactions [19]. The spectral patterns of the alkenes shown in Figure 4 are typical of those obtained throughout this work.

Hexane showed primarily  $[M - 1]^+$  ions and the mobility spectrum had no features in common with that of hexene, indicating that little alkene is formed if the stepwise mechanism is occurring. Both n-heptane and n-octane showed  $[M - 3]^+$  ions and shared common mobility peaks with corresponding alkenes. Thus, some of the ion-molecule clusters formed in both pairs have similar size-to-charge ratios. However, IMS alone cannot determine if the common peak represents the same ion-molecule cluster, so APCI-MS study of alkenes was undertaken.

### APCI-MS of Alkenes

APCI-MS analyses of four alkenes showed that fragmentation was the dominant ionization mechanism. Cyclohexene fragmented and yielded hydrated ions at  $m/z$  87 and an ion-molecule cluster of this ion was observed at  $m/z$  163. An  $M[M - 1]^+$  cluster was also detected. Three branched alkenes (2,2,4-trimethyl-2-pentene, 2-methyl-1-hexene, and 2-methyl-2-hexene) showed a similar propensity for fragmentation. The 2-methyl-1-hexene showed a fragment and dimer analogous to those observed in cyclohexene. Small amounts of  $[M + 1]^+$  ions were observed in the spectra of 2,2,4-trimethyl-2-pentene and 2-methyl-1-hexene, as consistent with findings of CIMS [6, 21].



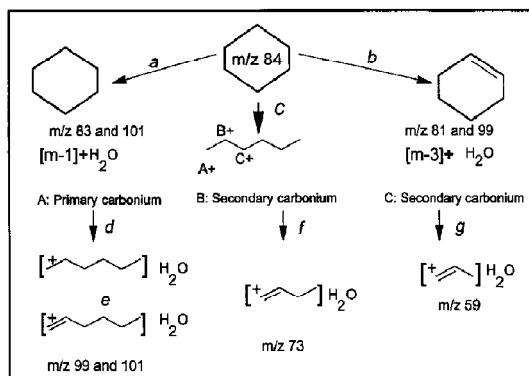
**Figure 4.** Comparison of selected alkane and alkene spectra: hexane (a) and 2-hexene (b), heptane (c) and 2-heptene (d), octane (e) and 2-octene (f). Axes and legends are identical to those in Figure 2.

#### Case Study: Hexane/Cyclohexane/Cyclohexene

Potential ionization pathways are not difficult to propose for the APCI of alkanes and alkenes. The interest here was to correlate APCI-MS results with mobility spectra, so cyclohexane, cyclohexene, and hexane were evaluated in a detailed study. Proposed APCI routes for cyclohexane and cyclohexene are presented in Figures 5 and 6. The mobility spectra of these compounds and n-hexane are shown in Figure 7.

Several assumptions were made in developing proposed ionization mechanisms. First, rearrangements of carbonium ions can occur and have been previously observed under CIMS conditions [22]. However, in the initial ionization, formation of more highly substituted carbonium ions will be favored. Consequently, abundances of primary carbonium ions will be lower than secondary and tertiary carbonium ions. Also, reactions that are energetically permissible or that have been previously reported under CIMS or APCI-MS conditions were considered. Finally, all proposed mechanisms assume low levels of moisture. Although most structures are shown as hydrated, hydrated and non-hydrated forms of the ions were often observed.

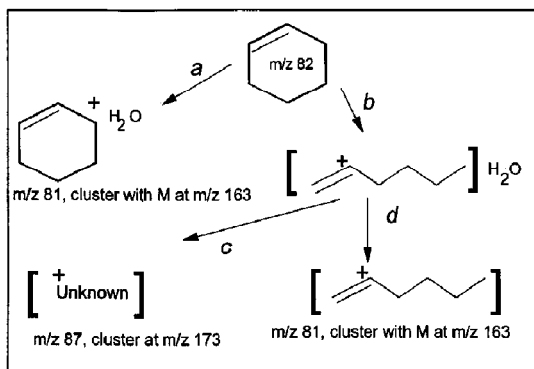
Cyclohexane and cyclohexene both showed ring breakage under APCI-MS conditions. Fragmentation of



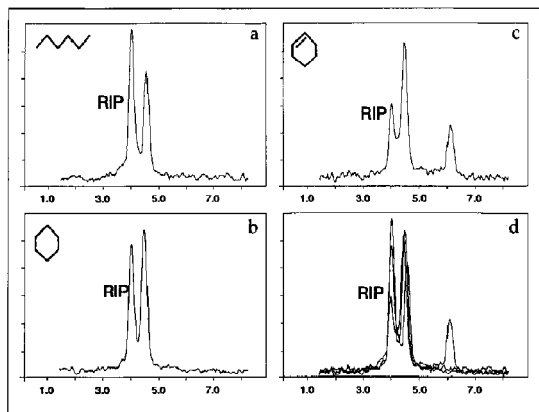
**Figure 5.** Proposed APCI-MS ionization of cyclohexane. Refer to the text for details. Lowercase letters identify specific structures and pathways referenced in the discussion.

the alkene was expected, but the ring breakage and fragmentation of the cyclohexane was not anticipated. Fragments at  $m/z$  59 and 73 dominated the APCI mass spectrum of cyclohexane and are indicative of ring breakage (formula c in Figure 5) that can produce three different carbonium ions (formulas d, f, and g). As expected, the dominate ions at  $m/z$  59 and 73 originated from the more stable carbonium ions. Hydrogen elimination was responsible for the ions given as formulas b, e, f, and g.

A primary carbonium ion (formulas d and e) and the intact ring (formulas a and b) are sources of  $[M-1]^+$  and  $[M-3]^+$ . These ions (formulas a, b, d, and e) cluster with water and can be detected as hydrated species. Unfortunately, the ratio of open and closed ringed structures could not be determined. CIMS studies of the cycloalkanes suggest the closed-ring ions will be energetically favored over open-ring ions [23]. Four-carbon ions or smaller should not be detected under standard IMS conditions in nitrogen if these pathways are general. Attempts to obtain response on VOA to methane through butane were unsuccessful



**Figure 6.** Proposed APCI-MS ionization of cyclohexene. Refer to the text for details.



**Figure 7.** Mobility spectra for (a) hexane, (b) cyclohexane, (c) cyclohexene, and (d) composite. These spectra were obtained from the VOA, axes as previously described. Drift times for the monomer peaks are 4.53, 4.45, and 4.45 ms for hexane, cyclohexane, and cyclohexene, respectively.

despite introduction of excessive quantities into the ionization region. Therefore, what can be detected are the closed chain species (formulas a and b) and the  $m/z$  99/101  $[M - 1]^+$  and  $[M - 3]^+$  chains (formulas d and e).

Ionization of cyclohexene conformed to pathways [21] illustrated in Figure 6. The ion  $[M - 1]^+$  was formed along with an unidentified hydrated fragment ion ( $m/z$  87). As with cyclohexane, the ratio of open and closed ring  $[M - 1]^+$  could not be determined. Ion-neutral clusters of the  $[M - 1]^+$  and fragment ions were observed, suggesting rapid formation and high stability in air. In contrast, no ion-neutral clusters of the molecular ion or fragments were detected in the APCI-MS of cyclohexene. These findings demonstrate that  $[M - 3]^+$  from cyclohexene was not created by a stepwise reaction via cyclohexene. For an alkene intermediate, fragment dimers should have been observed in the cyclohexene spectrum and were not detected.

Ion mobility spectra were used to determine which APCI pathways predominated under IMS conditions. APCI-MS of cyclohexene and hexene showed significant fragmentation and ring breakage, yet the mobility spectrum of cyclohexene (Figure 7b) showed a single peak without evidence of fragmentation, ring breakage, or an alkene intermediate. Mobilities of *n*-alkanes are lower than those of corresponding cyclic species owing to the ring's compactness. The drift time of the cyclohexane product ion was 4.45 ms and that of the *n*-hexane was 4.53 ms. If the cyclohexane fragments in the IMS, the mobility spectrum would have features consistent with that of hexene or hexane. Because mobilities did not match and because the cyclohexane spectrum showed no evidence of fragmentation, a closed-ring  $[M - 1]^+$  or  $[M - 3]^+$  moiety (formulas a and b in Figure 5) can be considered reasonable.

The mobility spectrum of cyclohexene (Figure 7c)

showed evidence of fragmentation in the spectral region between the reactant ion and monomer peaks. The elevated baseline is typical of formation of fragment ions smaller than the product ion but larger than ions of the reactant ion peak. A dimer peak was also observed in agreement with APCI-MS data. The drift time of the cyclohexene monomer and the cyclohexane monomer were identical, showing only that the size-to-charge ratios for the product ions were identical. These product ions are likely both cyclic  $[M - 1]^+$  with a difference of a double bond in the cyclohexene ring. The size difference between the cyclohexane and cyclohexene rings was too small to be resolved by using current IMS drift tube technology.

The mobility spectra of cyclohexane and cyclohexene confirm that a stepwise alkane  $\rightarrow$  alkene reaction did not occur in the IMS and that the  $[M - 3]^+$  of an alkane was not the same as the  $[M - 1]^+$  of the corresponding alkene. The cyclohexene mobility spectrum agreed with what would be expected if APCI-MS pathways shown in Figure 6 were followed. However, the cyclohexane mobility spectrum did not show evidence of fragmentation or dimer formation, indicating either  $[\text{cyclohexene-1}]^+$  did not form from cyclohexane or that the ion lifetime may have been too short to allow the alkene ionization pathway to proceed and for typical alkene mobility spectral features to develop. However, the high proton affinity of alkenes and the stability of the protonated species implies that if an alkene intermediate did form, unambiguous spectral evidence would result.

Correlations between the APCI-MS and mobility spectrum of cyclohexane were not as strong as correlations observed for cyclohexene. Notably, cyclohexane fragmentation seen in APCI-MS was not evident in the ion mobility spectrum. Thus, qualitative information on ionization is available from APCI-MS, but what exact mechanisms proceed in IMS can be determined only through analysis of the mobility spectrum. Even so, certain questions regarding ionization cannot be answered without IMS-MS data. For example, the monomer peak of cyclohexane in IMS was shown to be a cyclic species, most likely  $[M - 1]^+$ . To what extent a cyclic  $[M - 3]^+$  ion contributes to this peak cannot be determined given the current data.

### Formation of $[M - 1]^+$

The nature of the reaction by which  $[M - 1]^+$  is formed was addressed through existing and new APCI-MS and IMS data. In IMS two routes can lead to the formation of an  $[M - 1]^+$  ion: proton transfer (eq 1) and charge transfer (eq 2). Kojiro et al. [2] published ion mobility spectra obtained in dry helium and with metastable helium ionization. Those spectra were qualitatively similar to those obtained in the present work with well-defined product ion peaks and no evidence of fragmentation, while previous IMS studies of alkanes [4, 5] using moist nitrogen reported higher



detection limits (parts-per-million versus parts-per-billion in dry helium), contamination, and fragmentation. The similarity in spectral patterns between spectra obtained here and those obtained under dry helium conditions suggests the mechanisms occurring in dry nitrogen are similar to those occurring in dry helium. These observations agree with preliminary results reported by Kojiro et al. [2] of IMS of alkanes in dry air.

As water concentrations decrease, charge transfer reactions become increasingly important in product ion formation. Charge transfer reactions can be more efficient than proton transfer reactions, particularly when water concentrations are low and proton transfer reactions are no longer favored. For alkanes with low relative proton affinities, charge transfer reactions will yield far more product ions than proton transfer reactions. Decreasing the moisture in an APCI system also affects reactant ions. When reactant ions are minimally hydrated, acidity of the proton increases [9, 10]. This increase in acidity means that the proton is more accessible for proton transfer reactions. In this work, moisture levels were maintained below 1 ppm, which is lower than previously reported IMS studies of alkanes but higher than levels reported by Kojiro et al. [2]. Spectra resembling those obtained in dry helium were noted here without invoking rigorous moisture control procedures. The EVM was unmodified from the commercial design and employed only charcoal and molecular sieve filters to dry the carrier and drift gases. Similarly, gases for the VOA were treated with commercially available filters. Thus, IMS instruments can be designed to exploit performance improvements arising from low moisture conditions. Seemingly, the VOA and EVM were operated at moisture levels in which both charge transfer reactions and proton transfer reactions could occur, and low water concentrations enhanced both routes to product ion formation. An investigation into which pathway dominates at specific moisture concentrations is planned.

## Conclusions

Molecular structure of alkanes determines the size of the hydration sphere around the ion and thus indirectly determines how temperature will affect mobility. Moisture plays a significant role in determining the nature of the ion-molecule chemistry that occurs under APCI and IMS conditions. Improved performance of the mobility spectrometers in terms of spectral patterns and strength of response was attributed to increased acidity of the reactant ion protons and an increase in the number of successful charge transfer reactions favored under low moisture conditions. Ionization of alkanes under IMS conditions did not proceed through an alkene intermediate.

Consolidation of APCI-MS and IMS data was valuable for analysis of ionization pathways, considering the cost and scarcity of IMS-MS instrumentation. Procedures were demonstrated to compare APCI-MS and IMS results through APCI reactions and to use this information to interpret mobility spectra. The case study presented above using hexane, hexene, cyclohexane, and cyclohexene illustrates how APCI-MS, CIMS, IMS-MS, and IMS findings can be successfully integrated and exploited.

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