Information on the Location of Carbon-Carbon Double Bonds in C_6 — C_{23} Linear Alkenes from Carbon Addition Reactions in a Quadrupole Ion Trap Equipped with a Pulsed Sample-Inlet System

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Ion-molecule reactions of a number of alkene molecular ions with different neutral alkenes were studied in a quadrupole ion trap equipped with a pulsed sample-inlet system. The molecules studied include several isomeric unbranched hexenes, heptenes, octenes, and nonenes, as well as representative alkenes with ten, twelve, fourteen, and twenty-three carbon atoms. Transfer of structurally characteristic number of methylene units between the ionic and neutral reactants dominates the product distributions for all the alkenes studied, with the exception of 1-alkenes. Isomeric alkenes can be readily distinguished on the basis of their products from reactions with neutral alkenes. It is suggested that distonic intermediates are generated in these reactions, and that they fragment by alkene elimination after 1,2- and 1,5-hydride shifts. The ability to vary the reaction time, pressure of the neutral reagents, and the type of ions and neutral molecules present in the reaction chamber during each stage of the experiment sequence makes it possible to maximize the amount of structural information obtained for alkenes in these experiments. Use of CS_2^+ to generate the alkene molecular ion by charge exchange yields the same information without the need to carry out a mass-selection step for the ionized alkene. (*J Am Soc Mass Spectrom* 1991, 2, 305–313)

The problem of locating carbon-carbon double bonds in isomeric mono-olefins by mass spectrometry has been of interest for many years. The molecular ions of alkenes isomerize into a mixture of rapidly interconverting structures prior to fragmentation [1], and this isomerization is thought to be extensive even for nondecomposing ions after 10^{-5} seconds [1]. Therefore, mass spectrometric methods that do not deposit large amounts of energy in alkenes upon ionization and during the following reactions, or that are based on a neutral rather than on an ionized alkene, are potentially more successful in distinguishing isomeric alkenes than methods based on dissociation of activated ionized alkenes (e.g., electron ionization mass spectrometry, collision-activated dissociation). A number of studies have focused on low energy ion-molecule reactions for location of carbon-carbon double bonds, and promising methods based on this approach have appeared [2, 3]. For

example, the reactant ion NO^+ has been demonstrated to add to carbon-carbon double bonds to yield an intermediate ion that often gives characteristic fragments [4]. However, this method does not give conclusive results for carbon chains below C_{10} , and the product distributions obtained for long-chain alkenes are occasionally complex [2]. Problems involving other potentially useful chemical ionization reagents include limited selectivity (isobutane [2], ethylene oxide [2], dimethyl ether [2, 5], tetramethyl silane [2]), interfering ion-molecule reactions within the reagent gas system (tetramethyl silane [2], methyl vinyl ether [2, 6]), too extensive fragmentation and/or rapid isomerization of the ionized alkene (methane, tetramethyl silane) [2], and low sensitivity (amines [2]). The most promising methods thus far include complexing the alkene with Fe^+ , followed by collision-activated dissociation of the complex [7]. This approach results in dissociation products that are highly characteristic of the neutral alkene [7]. Moreover, the method is applicable to various different alkenes, dienes, and alkynes [7].

We report here examination of the analytical potential of ion-molecule reactions occurring between an

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ionized alkene and a neutral alkene in a Paul-type quadrupole ion trap. Paul-type ion traps [8] are mechanically simple devices and they possess several features that are especially well-suited for analytical applications employing ion-molecule reactions. The ability to vary reaction time and to mass-select the reactant ion [9] remarkably simplifies the product distributions. The relatively high pressure commonly used [8] in quadrupole ion traps (mtorr range) is beneficial when studying reactions that require multiple collisions or that have low cross-sections. When the ion trap is equipped with pulsed valves [10], it is possible to select the neutral as well as ionic reagents present in the trap during each reaction. This eliminates many interfering side reactions.

Ion-molecule reactions occurring in pure olefins, especially in systems higher than ethylene, are quite complex [11-15]. However, the product distributions from these reactions seem to be much more dependent on the structure of the ionic and neutral reactant alkenes than is the case for the fragmentation products obtained upon electron ionization of these alkenes [11]. Especially intriguing is the suggestion that there is no significant rearrangement in parent ions during the reaction. However, earlier studies suggest that the products obtained in reaction of an ionized alkene with a neutral alkene depend on the experimental conditions as well as on the structure and the energy content of the ionic and neutral reactants [11]. It is our interest to find out whether the conditions [16] prevailing in quadrupole ion traps [13, 17] are suitable for application of ion-molecule reactions in identification of specific structural features in ions and neutral molecules. The focus of this study is on analytically important, relatively long-chain alkenes ($> C_6$) that have not been studied before. These molecules include a series of isomeric hexenes, heptenes, octenes, and nonenes, as well as 5-decene, 1-dodecene, 7-tetradecene, and 9-tricosene.

Experimental

The experiments were carried out with a prototype Finnigan (San Jose, CA) quadrupole ion trap mass spectrometer described previously [18]. A modified

Figure 1. The sequence of radio-frequency (RF) and direct-current (DC) voltages used in the quadrupole ion trap to mass-select the reactant ion and to analyze the products (S). The two different times that were used to add neutral samples through the pulsed valve are also indicated (PV).

version of the commercial software was used to implement the necessary radio-frequency and direct-current voltage sequences (Figure 1) [9, 18]. Ions were generated by electron ionization unless otherwise specified. Application of appropriate radio-frequency and direct-current voltage pulses on the electrodes of the ion trap allowed isolation of the desired reactant ions, storage of the reactant ions and their ionic products during the reaction period, and analysis of all the ions present in the trap after the reaction period. Typical operation parameters used in this study are as follows: electron ionization time 0.4 msec, ion isolation time 4 msec, mass range of ions stored in the trap during the reaction period equal to or higher than m/z 40, and reaction time variable (typically 200 msec).

A General Valve Corporation (Fairfield, NJ) Series 9 pulsed valve with a commercial high voltage power supply and driver unit (IOTA, 1 General Valve Corporation) was used for pulsed reagent introduction [10]. The pulsed valve was used to introduce reagents either at the beginning of the pre-ionization time (a time interval just before electron ionization), or at the beginning of the reaction time.

All the samples were obtained commercially, and introduced in the mass spectrometer through

Table 1. The mass values of the main ionic species resulting from reactions of ionized alkenes with their neutral precursors^a

Alkene	$M^{+ \cdot}$	$(M - 2H)^{+ \cdot}$	Carbon addition products $(M + nCH_2)^{+ \cdot}$					
			$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$
E-2-nonene	126	<u>124</u>	<u>154</u>	<u>168</u>	<u>182</u>	<u>196</u>	<u>210</u>	
E-3-nonene	126	<u>124</u>		<u>168</u>	<u>182</u>	<u>196</u>	<u>210</u>	
Z/E-4-nonene	126	<u>124</u>		<u>168</u> [*]	<u>182</u>	<u>196</u>	<u>210</u>	
E-5-decene	140	<u>138</u>			<u>196</u>	<u>210</u>	<u>224</u>	<u>238</u> [*]
Z-5-decene	140	<u>138</u>			<u>196</u>	<u>210</u>	<u>224</u>	<u>238</u>

^{*}Very weak signal.

^aMajor products are underlined.

^bThe alkenes were ionized by electron ionization.

Granville-Phillips leak valves at a nominal pressure of $(8-10) \times 10^{-7}$ torr, unless otherwise specified. The nominal pressure of CS_2 was 8×10^{-7} torr, as read by an ionization gauge in the vacuum manifold. The nominal pressure of the helium buffer gas was 5×10^{-5} torr and the estimated pressure is 1×10^{-3} torr.

Results

Two different methods were used to ionize alkenes in the quadrupole ion trap. Table 1 shows the main ionic products obtained in reactions of selected alkenes with their molecular ions generated by 70-eV electron ionization (the main addition products are underlined). Table 2 shows the main ionic products obtained when CS_2^+ (recombination energy 10.1 eV) was used to ionize the alkenes by charge exchange. The product distributions obtained using these different ionization methods are similar. Positional isomeric alkenes give quite different product distributions while the geometrical isomers studied do not differ in their behavior. All the alkenes studied, with the exception of 1-alkenes, give relatively simple product distributions at long reaction times. The reaction of ionized 2-nonene with neutral 2-nonene, for example, yields exclusively the ions of m/z 124, 154, 168, 182, and 210 (Table 2) after 1000 msec reaction time. The product distribution obtained for ionized 4-nonene reacting with neutral 4-nonene after a 200 msec reaction time is shown in Figure 2a (excluding the ion that formally corresponds to loss of H_2 from ionized 4-nonene), and Figure 3 shows formation of the four most abundant product ions as a function of time for the reaction of ionized 4-nonene with 4-nonene. Figure 4 shows reaction products obtained for pure 3- and 4-nonenenes. Note that all the product ions observed in each case are odd-electron species, in spite of the fact that formation of even-electron fragments by loss of a hydrogen atom or alkyl radicals are usually among the lowest energy pathways for unimolecular dissociation of ionized alkenes [1, 13, 15]. Note that the reaction of ionized pentadienes with the corresponding neutral molecules have been examined previously in the quadrupole ion trap, and alkyl radical loss following dimerization is a significant pathway [19].

Several 1-alkenes were also studied. These molecules, 1-hexene (see Figure 5), 1-heptene, 1-octene, 1-nonene, and 1-dodecene, differ drastically in their behavior from all the other alkenes studied by producing very complex product distributions, and were excluded from Tables 1 and 2. The product distributions of 1-alkenes are not characterized by dominant transfer of CH_2 units as for the other alkenes. For 1-alkenes, formal transfer of CH and CH_3 units were also observed, and these reactions sometimes yielded more abundant products than CH_2 transfers that dominate for the other alkenes. The product distributions obtained for 1-alkenes do not follow the mechanistic rationale presented later in this article.

Figure 2. (a) Ionic products obtained from reactions of ionized 4-nonene with neutral 4-nonene in the quadrupole ion trap (reaction time 200 msec). (b) Ionic products obtained from reactions of ionized 4-nonene with neutral 4-nonene and neutral 2-nonene. 2-Nonene was pulsed in the trap after the ionization period (reaction time was 200 msec).

Figure 2b shows the carbon-addition products obtained in a cross-reaction where ionized 4-nonene was reacted with a mixture of neutral 4-nonene and neutral 2-nonene (reaction time 200 msec). Table 3 shows the carbon-addition products obtained in other cross-reactions. Ionized cyclohexene did not give carbon-addition products with neutral cyclohexene or with 7-tetradecene, and is not included in Table 3. Ionized cyclo-octene, on the other hand, produced carbon-addition cross-reaction products with neutral 4-nonene (Table 3). It is obvious from the results shown in Table 3 that the product distributions obtained in cross-reactions can be as simple as is obtained for each of the pure systems separately but there are reactant systems that give very complex product distributions. Pulsed sample introduction was used in several experiments to obtain more information about the reactions. These results are discussed in detail later in this article.

A carbon-addition product of 4-nonene, m/z 196 (from addition of five CH_2 units to 4-nonene), was mass-selected for further examination in the ion trap. This ion was found to be unreactive toward neutral 4-nonene. Collisional activation of this ion in the ion trap [18] (an MS/MS/MS experiment) yields several ionic dissociation products, and they all correspond to formal losses of neutral alkanes. The main fragments have mass values 152 (loss of propane), 138 (loss of butane), and 124 (loss of pentane). These fragments do not correspond to the carbon-addition products that are formed in ion-molecule reactions of alkenes (Tables 1-3).

Discussion

Reactions of small alkene radical cations with their neutral precursors have been studied extensively [11-15]. The major ionic products (with the exception of loss of a hydrogen molecule) obtained under low pressure in ion cyclotron resonance traps are the re-

Table 2. The mass values of the main ionic species resulting from reactions of ionized alkenes with their neutral precursors

Alkene	M ⁺⁺	(M - H) ⁺	(M - 2H) ⁺⁺	n = 1	n = 2	Carbon addition products (M + nCH ₂) ⁺⁺						
						n = 3	n = 4	n = 5	n = 6	n = 7	n = 8	n = 9
E-2-hexene	84	83	82		112	126						
E-3-hexene	84	83	82		112*	126						
Z-2-heptene	98	97	96		126	140	154					
Z-3-heptene	98		96		126	140	154					
E-2-octene	112	111	110		140	154	168	182				
E-2-nonene	126	125	124		154	168	182	196	210			
E-3-nonene	126	125	124		124	168	182	196	210			
Z/E-4-nonene	126	125	124		124	182	196	210	238			
Z-5-decene	140	139	138		138	196	210	224	280	294	308	322
7-tetradecene	196	195	194		194							
Z-9-tricosene	322		320	434 (+8CH ₂), 504 (+13CH ₂)	448 (+9CH ₂), 518 (+14CH ₂)	462 (+10CH ₂), 532 (+15CH ₂)	476 (+11CH ₂), 546* (+16CH ₂)	490 (+12CH ₂)				

*Very weak signal.

*Major products are underlined.

*The alkenes were ionized by CS₂ charge exchange.

Figure 3. The formation of the most abundant product ions as a function of reaction time for reaction of ionized 4-nonene (m/z 126) with neutral 4-nonene in the quadrupole ion trap. The ion of m/z 124 is formed in an ion-molecule reaction that results in a formal loss of H_2 from the ionized alkene; the ions of m/z 196, 182, and 210 arise from addition of five, four, and six CH_2 units to 4-nonene, respectively.

Figure 4. Ionic products obtained in reaction of (a) ionized 4-nonene with neutral 4-nonene and (b) ionized 3-nonene with neutral 3-nonene in the quadrupole ion trap. The reaction time was 200 msec.

sult of addition of one, two, or three carbon atoms to the parent backbone [11]. While these carbon atoms can carry zero, one, or two hydrogens, the most abundant products often involve transfer of methylene units [11]. This appears to apply to linear alkenes from ethylene through hexene [11], as well as to a number of other small alkenes [12-15]. Heinis [11] has

proposed a mechanism that explains qualitatively the carbon-addition product distributions. Support for this mechanism has been obtained in further studies using different experimental approaches [13]. The first step of the reaction involves pairing of the unpaired electron of the ionized alkene with a π -electron of the neutral alkene to give an intermediate adduct (ad-

Table 3. The main ionic carbon-addition products formed in cross-reactions of ionized alkenes with neutral alkenes in the quadrupole ion trap

Reactant ion(s)	Neutral alkene(s)	Product ions (m/z)	Experiment*
4-nonene,	4-nonene,	154	, 168, 182,
2-nonene	2-nonene	196, 210	
4-nonene,	2-nonene	154, 168,	4-nonene pulsed in
2-nonene		182, 196, 210	
4-nonene	4-nonene,	154, 168, 182,	2-nonene pulsed in
	2-nonene	196, 210	
4-nonene,	4-nonene	182, 196, 210	2-nonene pulsed in
2-nonene			
4-nonene	4-nonene,	140, 154, 168,	4-nonene pulsed in
	2-hexene	182, 196, 210	
4-nonene	2-hexene	140, 154, 168	4-nonene pulsed in
2-hexene	2-hexene,	112, 126, 140, 154,	
	4-nonene	168, 182, 196, 210	
2-hexene	4-nonene	182, 196	2-hexene pulsed in
			before ionization
1-hexene	4-nonene	182, 196, 210	1-hexene pulsed in
			before ionization
cyclo-octene	4-nonene	166, 180, 182,	cyclo-octene pulsed in
		196, 210	

*Stationary pressure of reagents was used unless otherwise mentioned

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tertiary carbon. The product ions are unreactive toward neutral alkenes (see Figure 3).

Earlier evidence supports [13,15] the suggestion that isomerization of the high energy intermediates takes place predominantly by 1,2-hydride shifts, and that these hydride shifts have a low activation barrier (6–12 kcal/mol) [22]. For the long-chain alkenes studied here, various long-range hydride shifts are also possible. 1,5-Hydride shifts apparently compete with 1,2-hydride shifts in these intermediates. The involvement of other long-range hydride shifts or several consecutive hydride shifts (e.g., 1,2-hydride shift followed by a 1,5-hydride shift) cannot be entirely excluded, although most of the results obtained here can be rationalized without involving other than 1,2- and 1,5-hydride shifts. The radical site may not participate in isomerization or fragmentation of the distonic intermediates. However, the localized odd spin probably limits or directs the hydride transfers occurring in the intermediates.

The intermediate adducts preferentially fragment by loss of neutral alkenes to give odd-electron ionic fragments (addition of CH_2 units). This finding supports the proposed distonic structures because it has been observed [23] earlier that distonic structures often preferentially fragment to give odd-electron ions in quadrupole ion traps, in contrast to conventional radical cations that mainly fragment to even-electron ions through the loss of neutral radicals. The proposal (Scheme I) that several or all of the product ions also have distonic structures is supported by the discovery of dominant odd-electron ionic dissociation products upon collisional activation of the ion of m/z 196 formed by addition of five CH_2 units to 4-nonene in reaction of ionized 4-nonene with neutral 4-nonene.

The major competing pathway to carbon-addition reactions is charge exchange between the ionized and the neutral alkene. Thus, while cross-reactions involving ionized 4-nonene and neutral 2-nonene generally yield all the ionic products formed in the pure systems separately, the reaction of ionized 2-nonene with

Scheme II

neutral 4-nonene only produces carbon-addition products characteristic for pure 4-nonene (Table 3). This result must be due to rapid, nearly thermoneutral charge exchange between 2-nonene (ionization potential 8.90 eV) and 4-nonene (ionization potential 8.8 eV [24]), followed by reaction of ionized 4-nonene with neutral 4-nonene to give the observed products. In an analogous manner, only products characteristic for the pure 4-nonene system were obtained from reactions of ionized 1-hexene with 4-nonene (Table 3). In this case, electron exchange between ionized 1-hexene (ionization potential 9.44 eV) and neutral 4-nonene (ionization potential 8.8 eV) is 0.64 eV exothermic [24].

The cross-reactions involving 2-hexene and 4-nonene were examined systematically (Table 3). Scheme II summarizes our conclusions. When ionized 2-hexene (ionization potential 8.97 eV) is allowed to react with a mixture of neutral 2-hexene and 4-nonene, collisions with neutral 2-hexene result in carbon-addition products characteristic for the pure 2-hexene system (Table 2), and collisions with 4-nonene lead to charge exchange (exothermic [21] by 0.17 eV) and formation of ionized 4-nonene. Ionized 4-nonene then reacts with neutral 4-nonene to give products characteristic for the pure 4-nonene system, and with neutral 2-hexene to give the expected cross-reaction products. Support for this reaction sequence is provided by the following observations. When 2-hexene was pulsed in the trap before ionization so that molecular ions of 2-hexene were generated and trapped but neutral 2-hexene was pumped away before the reaction of ionized 2-hexene with neutral 4-nonene was examined, only products characteristic for the pure 4-nonene system were obtained. When 4-nonene was ionized and allowed to react with neutral 2-hexene without neutral 4-nonene in the trap during the reaction time (4-nonene pulsed in before ionization time), only the cross-reaction products were obtained. And finally, when ionized 4-nonene was allowed to react with both 2-hexene and 4-nonene (2-hexene pulsed in before reaction time), the cross-reaction products as well as the products characteristic for the pure 4-nonene system were obtained.

In agreement with numerous earlier results [11, 12] 1-olefins were found to be the most reactive systems

and to give more complex product distributions than other olefins in our experiments (see Figure 5). Structurally characteristic carbon-addition products do not dominate the product distributions of 1-alkenes. Several factors may account for this behavior, including the fact that formation of the intermediate adducts is more exothermic for 1-alkenes than for other alkenes [11], making skeletal rearrangements within the intermediates of 1-alkenes more likely. Further, because the heat of formation of ionized 1-alkenes is significantly higher than that of other alkenes, ionized 1-alkenes are more likely to rearrange [14] to a mixture of isomeric ionized alkenes and distonic ions prior to bimolecular reactions. From an analytical point of view, the distinctly different behavior observed for 1-alkenes, whatever the underlying reasons, is quite desirable because it allows distinction of these molecules from all other alkenes. However, this procedure would not be useful if it were not known in advance that the analyte was an alkene.

As a summary, our findings are in agreement with the earlier description [11] of the general features of carbon-addition reactions of small ionized alkenes with neutral alkenes. Specifically, our results indicate that (1) no significant rearrangement occurs in the parent ions prior to or during the reaction, (2) addition occurs at either end of the double-bond, as long as a primary carbocation is not produced, (3) no skeletal rearrangement occurs in the intermediate adduct, (4) fragmentation involving more than one bond is not likely, and (5) fragmentation occurs most favorably at the tertiary carbon in the intermediate. For long-chain alkenes, relatively fast 1,5-hydrogen shifts apparently compete with 1,2-hydrogen shifts and lead to a number of reaction products that are not accessible for smaller alkenes. Furthermore, long-chain alkenes seem to be more selective in their reactions than has been observed earlier for smaller species.

The analytically most promising reagent ion studied here is ionized cyclo-octene because this ion does not produce carbon-addition products with its neutral precursor. Moreover, ionized cyclo-octene does not add carbon units to other alkenes, but can only receive them (Table 3). If cyclo-octene is pulsed in the trap before the ionization period, the products from ion-molecule reactions between ionized cyclo-octene and neutral cyclo-octene can be eliminated, and only the ionic products characteristic for the structure of the analyte alkene are observed.

Conclusions

The conditions prevailing in Paul-type quadrupole ion traps using He buffer gas are well-suited for using ion-molecule reactions in structural studies of ions and neutral molecules. The product distributions obtained in the reactions of the molecular ions of fourteen different alkenes with neutral alkenes, with the

exception of 1-alkenes, are remarkably simple and structurally characteristic. Only one abundant product ion series, [alkene + $n\text{CH}_2^+$], is formed as the terminal product in each case. The number (n) of methylenes transferred between the ionized and neutral alkene is a reflection of the position of the double bond in both reagents. These product ions are readily distinguished from other reaction products because they are radical cations. The selectivity of the ion-molecule reactions studied is explained, at least partially, by the expectation that ion-molecule association reactions involving large ionic species are less exothermic than those involving smaller ions [9]. It follows that the larger intermediate adducts will have an energetically more limited selection of pathways available for them [9]. Further, our results indicate that stable long-chain alkene molecular ions generated by electron ionization CS_2 -charge exchange have not entirely lost their structural identity upon ionization or during storage in the Paul-type quadrupole ion trap, and the same applies to the intermediate adducts obtained from addition of an ionized alkene to a neutral alkene.

A useful procedure for analytical applications involving location of carbon-carbon double bonds in long-chain alkenes could begin with introducing cyclo-octene in the ion trap through a pulsed valve, ionizing it by charge exchange with CS_2^+ , and examining its reactions with the analyte. This remarkably simple and selective method has the additional advantage that no mass selection of an alkene is required. Further investigations concerning analytical applications of the reactions discussed and the generality of the approach for carbon-carbon double bond location are in progress.

Acknowledgments

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