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Unimolecular Photochemistry of *n*-Alkenes Studied by Photodissociation–Photoionization Mass Spectrometry

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The 193-nm unimolecular photochemistry of *n*-alkenes from C₅ to C₁₄ is studied by photodissociation–photoionization mass spectrometry (PDPI/MS). In PDPI/MS, a UV laser induces neutral unimolecular photodissociation. The resulting neutral fragments and any remaining parent molecules are then softly ionized with coherent vacuum UV radiation and mass analyzed. Photodissociation of *n*-alkenes is dominated by cleavage of the β C–C bond. Products of α - and γ -cleavage are typically less than 20% as abundant as the β -cleavage fragments. Secondary fragmentation of the primary products occurs both by neutral fragmentation during photodissociation and by ionic fragmentation during photoionization. The energetics of the neutral secondary reactions indicate that between 400 and 500 kJ/mol is consumed during photodissociation. The abundances of many secondary fragmentation products decrease with increasing molecular size. Because neutral fragmentation occurs without significant isomerization, PDPI/MS provides structural information that is not available from ionic fragmentation in conventional mass spectrometric experiments. (*J Am Soc Mass Spectrom* 1993, 4, 65–72)

In photodissociation–photoionization mass spectrometry (PDPI/MS), neutral unimolecular fragmentation is induced by absorption of a UV photon. The photodissociation products and any remaining parent molecules are then softly ionized with coherent vacuum UV radiation and mass analyzed [1]. The resulting mass spectrum is characteristic of neutral rather than ionic fragmentation. By probing neutral fragmentation, PDPI/MS provides useful structural information that is not available from conventional mass spectra. PDPI/MS is also useful for studying unimolecular photochemistry because the fragmentation products do not undergo ion-molecule reactions or collisional deactivation. As a result, PDPI/MS fragmentation patterns are often easier to interpret than the product distributions from photochemical experiments in high-pressure cells.

For aliphatic compounds, a critical difference between ionic and neutral fragmentation is that radical cations usually have lower rearrangement barriers than their neutral precursors. As a result, neutrals are less likely than ions to undergo rearrangement prior to

fragmentation [1, 2]. When rearrangement does occur prior to fragmentation, it is difficult or impossible to distinguish the mass spectra of structural isomers.

Photochemical experiments in high-pressure cells under static (nonflow) conditions show that small alkenes undergo preferential cleavage at the β C–C bond when exposed to vacuum UV radiation [3]. The products of this cleavage reaction, an allylic radical and its saturated radical complement, are formed with little or no rearrangement [4]. Alkene radical cations, however, often undergo hydrogen atom rearrangement prior to ionic fragmentation [5]. This rearrangement changes the double-bond location, and structural information is lost. Because neutral photodissociation occurs without rearrangement, soft ionization of the products results in a mass spectrum that can be used to determine the location of the double bond [1]. For example, β -cleavage of 1-pentene produces allyl (C₃H₅) and ethyl (C₂H₅) radicals, whereas β -cleavage of 2-pentene produces methylallyl (C₄H₇) and methyl (CH₃) radicals.

In this report, the 193-nm photochemistry of *n*-alkenes from C₅ to C₁₄ is studied by PDPI/MS. The predominant photodissociation pathway observed is cleavage of the β C–C bond. The primary products undergo secondary fragmentation through both neu-

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tral and ionic channels. Wavelength-dependent photoionization is used to distinguish and interpret these secondary processes.

Experimental

The instrumentation used for PDPI/MS has been described previously [1, 6, 7]. The sample is introduced into the mass spectrometer by a room-temperature molecular leak and photodissociated with 5 mJ of 193-nm (6.42 eV, 620 kJ/mol) radiation from a Questek (Billerica, MA) Model 2110 excimer laser focused to a 3-mm² spot. During photodissociation, the backing plate of the mass spectrometer is held at ground and the first grid at +2500 V to remove ions produced by multiphoton absorption. After approximately 1 μ s, the backing plate is pulsed to +3750 V with a Velonex (Santa Clara, CA) Model 350 high-voltage pulse generator. The neutral photodissociation products and any remaining parent molecules are ionized with coherent vacuum UV radiation and detected by a 1-m time-of-flight mass spectrometer. The resulting transient signal is averaged with a Nicolet (Madison, WI) Model 450 Digital Oscilloscope. A California Avionic Laboratory Inc. (Campbell, CA) Model 123 digital delay generator controls the timing of the high-voltage and laser pulses. The high-voltage pulse sequence induces ringing in the low-mass region of the spectra (Figure 1).

The tunable, coherent vacuum UV radiation used for photoionization is generated by third harmonic conversion in various rare gas mixtures [8, 9]; 118.2-nm (10.49 eV) radiation is generated by frequency tripling the third harmonic of a Nd:YAG laser (Spectra-Physics GCR-3, Mountain View, CA) in a mixture of xenon and argon [10]. 120–129-nm (10.3–9.61 eV) radiation is generated by frequency tripling tunable UV radiation in various rare gas mixtures, as described previously [6].

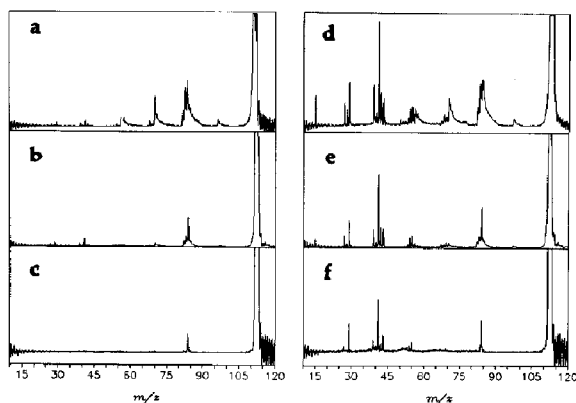


Figure 1. 1-Octene photoionization mass spectra at (a) 10.49 eV ($\times 10$), (b) 10.21 eV ($\times 10$), and (c) 9.68 eV ($\times 20$). 1-Octene photodissociation-photoionization mass spectra at (d) 10.49 eV ($\times 10$), (e) 10.21 eV ($\times 10$), and (f) 9.68 eV ($\times 20$).

The relative abundances of the PDPI/MS fragment ions in Tables 1–6 are calculated with respect to the area of the most intense PDPI fragment ion. The radical cation of the parent molecule and any ionic fragmentation products produced by photoionization of the parent molecule are excluded from Tables 1–6. The most intense PDPI fragment ion is used as the base peak to eliminate effects caused by variations in the absorption cross section of the different parent molecules at 193 nm and by changes in the overlap of the two lasers. This does not, however, account for variations in the ionization cross section of different neutral fragments. The absolute intensities of the neutral fragments observed with PDPI/MS are strongly dependent on the 193-nm absorption cross section of the parent molecule and the alignment of the two lasers. Under typical experimental conditions, the abundance of the most intense PDPI fragment ion is between 10% and 100% that of the ionized parent molecule. The uncertainty in the peak area is typically $\pm 2\%$ of the area of the most intense photodissociation peak, and the 3σ detection limit is typically between 1% and 5% relative abundance.

Most chemicals were purchased from Aldrich (Madison, WI), except 3-octene (Pfaltz and Bauer, Waterbury, CT). All were used without further purification.

Heats of formation and ionization potentials were obtained from the National Institute of Standards and Technology (NIST) Structures and Properties Database and Estimation Program, Version 1.2 (NIST, Gaithersburg, MD). When literature values were not available, the heats of formation were estimated by using Benson's additivity method [11]. The heats of formation for α -cleavage products of 2- and 3-alkenes were calculated by using a bond energy of 460 kJ/mol for the C=C–H bond [12]. The heats of reaction are not necessarily the same as the activation energies or appearance potentials for a particular process in our mass spectrometer, but they do indicate what mechanisms are energetically feasible.

Results

Figure 1 shows the photoionization (Figure 1, a–c) and the PDPI (Figure 1, d–f) mass spectra of 1-octene at different photoionization energies. As the photoionization energy decreases, the amount of ionic fragmentation from the parent ion and the amount of secondary ionic fragmentation of the photodissociation fragments decrease. This simplifies the mass spectra and facilitates identification of neutral photodissociation products. The trade-off is that products with high ionization potentials are not detected. The most intense photodissociation fragment is the allylic β -cleavage radical C_3H_5 , observed at m/z 41. The other fragments observed are formed by secondary fragmentation of the saturated radical and loss of H_2 from C_3H_5 .

Table 1. Relative abundances for PDPI/MS of 1-alkenes^a

1-Alkene	Formula (<i>m/z</i>)											
	CH ₃ (15)	C ₂ H ₃ (27)	C ₂ H ₄ (28)	C ₂ H ₅ (29)	C ₃ H ₃ (39)	C ₃ H ₅ (41)	C ₃ H ₆ (42)	C ₃ H ₇ (43)	C ₄ H ₅ (53)	C ₄ H ₆ (54)	C ₄ H ₇ (55)	C ₅ H ₉ (69)
10.49-eV photoionization												
1-Pentene	13	39	1	60	100	83	7	1	4	15	5	— ^b
1-Hexene	16	10	8	18	64	100	1	7	3	22	8	—
1-Heptene	42	5	8	49	69	100	—	—	—	20	20	—
1-Octene	8	25	28	52	46	100	33	28	7	15	20	—
1-Nonene	2	8	8	46	23	100	31	68	2	18	41	—
1-Decene	10	16	25	47	32	100	22	90	3	17	65	—
1-Undecene	3	9	8	27	16	47	17	100	2	14	55	11
1-Dodecene	9	6	9	21	15	36	19	100	1	9	59	13
1-Tridecene	15	4	5	12	7	24	17	100	1	10	57	21
1-Tetradecene	6	3	8	16	6	30	17	100	—	11	62	27
10.21-eV photoionization												
1-Pentene	7	27	1	60	70	100	5	—	4	30	4	—
1-Hexene	15	13	1	21	34	100	5	5	4	16	10	—
1-Heptene	—	—	—	51	23	100	—	—	—	14	22	—
1-Octene	6	14	3	35	20	100	23	22	4	13	17	5
1-Nonene	—	6	—	39	10	100	37	64	2	16	34	4
9.68-eV photoionization												
1-Pentene	—	23	—	79	41	100	—	—	—	20	5	—
1-Hexene	—	—	—	—	20	100	—	—	3	8	15	—
1-Heptene	—	1	—	36	4	100	—	—	—	9	15	—
1-Octene	—	7	—	59	23	100	9	34	—	4	8	—
1-Nonene	—	2	—	25	3	100	11	27	—	10	15	3
1-Decene	—	—	—	26	6	100	14	56	—	17	50	5
1-Undecene	—	—	—	24	7	66	19	100	—	20	51	12
1-Dodecene	—	—	—	12	4	36	20	100	—	12	69	30
1-Tridecene	—	—	—	4	2	21	18	100	—	11	58	25
1-Tetradecene	—	—	—	—	—	18	—	100	—	—	57	38

^aRelative to most intense photodissociation peak; ionic fragmentation of parent molecule is not included.

^bNo peak observed, typically less than 1%–5% abundance.

Table 2. Relative abundances for PDPI/MS of 2-alkenes^a

2-Alkene	Fragment (<i>m/z</i>)											
	CH ₃ (15)	C ₂ H ₃ (27)	C ₂ H ₄ (28)	C ₂ H ₅ (29)	C ₃ H ₃ (39)	C ₃ H ₅ (41)	C ₃ H ₆ (42)	C ₃ H ₇ (43)	C ₄ H ₅ (53)	C ₄ H ₆ (54)	C ₄ H ₇ (55)	C ₅ H ₉ (69)
10.49-eV Photoionization												
2-Pentene	100	40	6	74	62	26	—	—	21	92	40	—
2-Hexene	7	38	6	100	32	10	—	—	13	39	45	—
2-Heptene	16	38	17	100	44	35	4	11	21	35	92	1
2-Octene	5	17	17	100	19	25	5	5	13	15	62	1
2-Nonene	10	23	13	90	21	42	42	56	14	23	100	7
9.68-eV Photoionization												
2-Pentene	15	14	—	40	35	16	—	—	10	100	56	—
2-Hexene	—	17	—	100	19	11	—	—	6	30	61	—
2-Heptene	4	13	—	43	17	28	3	16	8	15	100	—
2-Octene	—	4	—	66	11	23	1	3	5	15	100	—
2-Nonene	—	4	—	34	5	18	7	29	4	12	100	2

^aRelative to most intense photodissociation peak; ionic fragmentation of the parent molecule is not included.

Table 3. Relative abundances for PDPI/MS of 3-alkenes^a

3-Alkene	Formula (<i>m/z</i>)												
	CH ₃ C ₂ H ₃ (15)	C ₂ H ₃ C ₂ H ₄ (27)	C ₂ H ₄ C ₂ H ₅ (28)	C ₂ H ₅ C ₃ H ₃ (29)	C ₃ H ₃ C ₃ H ₅ (39)	C ₃ H ₅ C ₃ H ₆ (41)	C ₃ H ₆ C ₃ H ₇ (42)	C ₃ H ₇ C ₄ H ₅ (43)	C ₄ H ₅ C ₄ H ₆ (53)	C ₄ H ₆ C ₄ H ₇ (54)	C ₄ H ₇ C ₅ H ₈ (55)	C ₅ H ₈ C ₅ H ₉ (68)	C ₅ H ₉ (69)
10.49-eV Photoionization													
3-Hexene	46	14	3	23	22	20	—	1	7	100	23	14	2
3-Heptene	34	27	13	74	27	44	2	4	10	100	19	13	7
3-Octene	57	28	16	36	22	100	9	32	13	97	30	26	27
3-Nonene	21	9	13	66	10	100	12	14	8	64	35	15	32
9.68-eV Photoionization													
3-Hexene	17	7	2	22	17	10	1	—	4	100	14	6	2
3-Heptene	2	9	—	96	14	23	—	—	5	100	17	8	5
3-Octene	—	11	1	31	14	87	5	40	6	100	33	17	32
3-Nonene	3	4	2	80	5	100	5	12	6	71	32	14	51

^aRelative to most intense photodissociation peak; ionic fragmentation of the parent molecule is not included.

β-Cleavage

The relative abundances of the PDPI/MS fragment ions are shown in Tables 1-4 for 1-, 2-, 3-, and 4-alkenes, respectively. The predominant fragment observed is the allylic radical produced by *β*-cleavage. Cleavage at the *β* C-C bond to produce an allylic radical requires less energy (ΔH_{rxn} = ca. 300 kJ/mol) than fragmentation at other locations. The *β*-cleavage product of 1-alkenes is the allyl C₃H₅[•]. The *β*-cleavage product of 2-alkenes is the methallyl C₄H₇[•]. The 3-alkenes have two *β*-cleavage sites; a single *β*-cleavage at the C₅-C₆ bond produces C₅H₉[•], and a second *β*-cleavage at the C₁-C₂ bond produces C₄H₆[•]. The product corresponding to *β*-cleavage at just the C₁-C₂ position to produce CH₃[•] is not unambiguously observed. The ion CH₃⁺ is observed but could be formed by several different processes. The corresponding alkenyl radical probably undergoes complete secondary fragmentation to form C₄H₆. The 4-alkenes also have two *β*-cleavage sites. The main fragmentation observed is *β*-cleavage at both sides to produce C₄H₆. A single *β*-cleavage in 4-nonene produces either C₆H₁₁[•], which is observed, or C₈H₁₃[•], which is not observed. The allylic *β*-cleavage products observed in

PDPI/MS clearly identify the location of the carbon-carbon double bond.

α-Cleavage

All 2-alkenes undergo *α*-cleavage to produce C₃H₅[•]; 9.68-eV photoionization gives an apparent branching ratio of 0.2 for *α*-cleavage relative to *β*-cleavage. This value assumes that the ionization cross section for the *α*- and *β*-cleavage products are equal, that the products do not undergo secondary fragmentation, and that the saturated radical for larger alkenes does not form C₃H₅[•] by secondary fragmentation. The unsaturated *α*-cleavage fragment of 3-alkenes (C₄H₇[•]) is observed in the PDPI/MS spectra and accounts for approximately 15% of the primary neutral fragmentation (Table 5). The *α*-cleavage product of 4-alkenes (C₅H₉[•]) is observed, but the abundance is less than 5% that of C₄H₆, the product of *β*-cleavage at both sites. Photolysis of 3-hexene in a high-pressure cell also produces *α*-cleavage, but the quantum yield is only 0.05 [16].

Although ionized product of 1-alkene *α*-cleavage (C₂H₃⁺) is observed with 10.49-eV photoionization, the abundance is strongly dependent on the photoioniza-

Table 4. Relative abundances for PDPI/MS of 4-alkenes^a

4-Alkene	Formula (<i>m/z</i>)												
	CH ₃ C ₂ H ₃ (15)	C ₂ H ₃ C ₂ H ₄ (27)	C ₂ H ₄ C ₂ H ₅ (28)	C ₂ H ₅ C ₃ H ₃ (29)	C ₃ H ₃ C ₃ H ₅ (39)	C ₃ H ₅ C ₃ H ₆ (41)	C ₃ H ₆ C ₃ H ₇ (42)	C ₃ H ₇ C ₄ H ₅ (43)	C ₄ H ₅ C ₄ H ₆ (53)	C ₄ H ₆ C ₄ H ₇ (54)	C ₄ H ₇ C ₅ H ₈ (55)	C ₅ H ₈ C ₆ H ₁₁ (69)	C ₆ H ₁₁ (83)
10.49-eV Photoionization													
4-Octene	12	25	10	100	11	32	2	4	5	97	23	7	—
4-Nonene	16	26	10	58	12	69	14	33	3	100	61	9	6
9.68-eV Photoionization													
4-Octene	—	6	1	100	9	17	1	2	1	88	20	4	2
4-Nonene	—	13	1	100	9	36	4	41	2	84	38	5	4

^aRelative to most intense photodissociation peak; ionic fragmentation of the parent molecule is not included.

Table 5. 3-Alkene energetics and apparent yield for neutral fragmentation products^a

Alkene	α -Cleavage ($C_4H_7^+$)			β -Cleavage ($C_5H_9^+$)			β -Cleavage followed by rearrangement ($C_3H_5^+$)			Two successive β -cleavages ($C_4H_6^+$)		
	ΔH_{rxn}	9.68	10.5	ΔH_{rxn}	9.68	10.5	ΔH_{rxn}	9.68	10.5	ΔH_{rxn}	9.68	10.5
	(kJ/mol) ^b	(eV) ^c	(eV) ^c	(kJ/mol) ^b	(eV) ^c	(eV) ^c	(kJ/mol) ^b	(eV) ^c	(eV) ^c	(kJ/mol) ^b	(eV) ^c	(eV) ^c
3-Hexene	411	0.11	0.16	301	0.01	0.00	412	0.08	0.14	452	0.80	0.70
3-Heptene	414	0.12	0.11	293	0.04	0.04	403	0.16	0.26	444	0.69	0.59
3-Octene	414	0.13	0.12	301	0.13	0.11	422	0.35	0.39	452	0.40	0.38
3-Nonene	410	0.13	0.22	293	0.20	0.11	404	0.39	0.45	444	0.28	0.22

^aYield expressed as a fraction of the sum of the four main fragments ($C_5H_9^+$ + $C_4H_7^+$ + $C_3H_5^+$ + $C_4H_6^+$).^bFor formation of the neutral product.^cPhotoionization energy.

tion wavelength. The corresponding neutral fragment (C_2H_3) has an ionization potential of 8.9 eV, but $C_2H_3^+$ is not observed with 9.68-eV photoionization. This indicates that the $C_2H_3^+$ in the 10.5-eV photoionization spectra is formed by secondary ionic fragmentation. This is surprising because Deslauriers et al. [4] report a yield of 0.11 for α -cleavage relative to β -cleavage of 1-hexene with 184.9-nm photolysis under static conditions. This yield is much higher than can be accounted for with 9.68-eV photoionization where $C_2H_3^+$ is not observed ($\Phi \leq 0.04$).

γ -Cleavage

All 1-alkenes undergo γ -cleavage to produce $C_4H_7^+$. In the PDPI/MS spectra of 1-hexene, both $C_4H_7^+$ and its

complement ($C_2H_5^+$) are observed with similar abundance and yield 0.1 for γ -cleavage relative to the allylic β -cleavage fragment. The ion $C_4H_7^+$ is also present for larger alkenes, but secondary fragmentation of the saturated β -cleavage radical inflates the apparent yield. In high-pressure photolysis experiments, a relative yield of 0.17 is observed for γ -cleavage of 1-hexene, and the results suggest that molecular isomerization contributes to this value [4].

Secondary Fragmentation

Small, saturated radicals produced directly by β -cleavage (C_2H_5 and C_3H_7) are usually observed intact. In larger alkenes, however, the saturated radical undergoes secondary fragmentation. Secondary loss of

Table 6. Fragmentation energetics for 1-octene

Ion	Relative abundance ^a			Fragmentation	ΔH_{rxn} (kJ/mol)	IP/AP ^c (eV)
	9.68 (eV) ^b	10.2 (eV) ^b	10.49 (eV) ^b			
C_2H_3	7%	14%	25%	Neutral: $M \rightarrow C_2H_3 + C_6H_{13}$	354	8.9
				$\rightarrow C_3H_5 + C_3H_6 + C_2H_3 + H_2$	530	8.9
				Ionic: $C_2H_5 \rightarrow C_2H_3^+ + H_2$		10.43
C_2H_4	0%	3%	28%	Neutral: $M \rightarrow C_3H_5 + C_2H_4 + C_3H_7$	397	10.51
				$M \rightarrow C_3H_5 + 2C_2H_4 + CH_3$	494	10.51
				Ionic: $C_6H_{11} \rightarrow C_2H_4^+ + C_3H_7$		11.52
C_2H_5	59%	35%	52%	Neutral: $M \rightarrow C_3H_5 + C_3H_6 + C_2H_5$	382	8.4
				Ionic: $C_6H_{11} \rightarrow C_3H_6 + C_2H_5^+$		9.26
C_3H_3	23%	20%	46%	Neutral: $M \rightarrow C_3H_3 + H_2 + C_5H_{11}$	476	8.69
				Ionic: $C_3H_5 \rightarrow C_3H_3^+ + H_2$		10.52
C_3H_5	100%	100%	100%	Neutral: $M \rightarrow C_3H_5 + C_5H_{11}$	299	8.13
C_3H_6	9%	23%	33%	Neutral: $M \rightarrow C_3H_5 + C_3H_6 + C_2H_5$	382	9.73
				Ionic: $C_6H_{11} \rightarrow C_3H_6^+ + C_2H_5$		10.59
C_3H_7	34%	22%	28%	Neutral: $M \rightarrow C_3H_5 + C_2H_4 + C_3H_7$	397	8.09
				Ionic: $C_6H_{11} \rightarrow C_2H_4 + C_3H_7^+$		9.11

^aAbundance relative to most intense photodissociation peak.^bPhotoionization wavelength.^cAppearance potential (AP) based on ΔH_{rxn} for the ionic fragmentation process; IP, ionization potential.

H₂ is often observed with 10.49-eV photoionization. The ions C₂H₃⁺ and C₃H₃⁺, apparently formed by loss of H₂ from C₂H₅⁺ and C₃H₅⁺ during photoionization, are present in most spectra. Although H⁺ loss requires a significant amount of energy, it is observed when the product formed has a conjugated double-bond system. The energetics and wavelength dependence of secondary fragmentation are discussed in detail in the Discussion section.

The 3-alkenes exhibit a number of interesting secondary fragmentation processes. After an initial β -cleavage to produce C₅H₉, they undergo a second β -cleavage to form 1,3-butadiene or a low-energy rearrangement reaction to form C₇H₄ and C₃H₅. The predominant ion observed is C₄H₆⁺, but as the alkyl chain length increases from 3-hexene to 3-nonene, the abundance of C₅H₉⁺ increases from 0.01 to 0.20, and the abundance of C₃H₅⁺ increases from 0.08 to 0.39 with 9.68-eV photoionization.

Discussion

The fragmentation observed in PDPI/MS could be caused by a number of mechanisms, including (1) absorption of a single 193-nm photon, (2) absorption of a second 193-nm photon by a primary photodissociation product, (3) ionic fragmentation during the photoionization step, and (4) neutral loss from ions produced by multiphoton ionization during the photodissociation step. The neutral fragmentation observed is consistent with a one-photon dissociation process. Although two-photon processes have been demonstrated in other systems [13], the abundances of the PDPI/MS fragments are constant relative to each other as the excimer laser pulse energy is varied. Because the excimer pulse energy can only be varied by a factor of 2 with the current experimental setup, a detailed power dependence cannot be preformed.

Ions formed by photoionization of the parent molecule are readily identified from photoionization mass spectra. As seen in Figure 1, a-c, the amount of ionic fragmentation is significantly reduced when less energetic photoionization is used. It is more difficult to distinguish ionic fragmentation of the photodissociation products from neutral secondary fragmentation that occurs prior to the ionization step. If a secondary fragment is formed as a neutral product, the relative abundance of the corresponding ion will not be strongly dependent on the photoionization energy above the ionization potential. If, however, an ion is formed by ionic secondary fragmentation during photoionization, its relative abundance should be strongly dependent on the photoionization energy near the appearance energy. If this appearance energy for ionic fragmentation is above the ionization potential of the corresponding neutral product, then these processes can be distinguished. This argument assumes that the radical photoproducts are not produced in highly excited states and that the appearance potentials for the fragmen-

tation products are similar to $\Delta H_{r,xn}$. Because the internal energy of the radical photoproducts and the appearance potentials for these fragmentation processes are not known, there is some ambiguity in identifying the observed secondary fragmentation processes as neutral or ionic.

Secondary Fragmentation Products

The saturated radical produced by β -cleavage is only observed with small alkenes. For larger alkenes, the energetics for neutral and ionic formation of secondary products and the relative abundances of these products with different photoionization energies suggest that much of the secondary fragmentation occurs prior to ionization. To illustrate this, the secondary fragmentation energetics and relative abundances for 1-octene are summarized in Table 6. β -Cleavage of 1-octene requires 299 kJ/mol, approximately half of the energy available from a single 193-nm (620 kJ/mol) photon. Although the saturated radical produced by β -cleavage of 1-octene (C₅H₁₁[•]) is not observed intact, several likely secondary fragments (C₂H₄, C₂H₅[•], C₃H₆, and C₃H₇[•]) are observed as ions in the mass spectra. β -Cleavage followed by secondary fragmentation of C₅H₁₁[•] to form C₂H₄ and C₃H₇[•] requires a total of 397 kJ/mol, whereas formation of C₂H₅[•] and C₃H₇[•] requires 382 kJ/mol. The relative abundances of C₂H₅⁺ (ionization potential 8.4 eV) and C₃H₇⁺ (ionization potential 8.1 eV) show little photoionization energy dependence. The relative abundances of C₂H₄ and C₃H₆ do show a strong wavelength dependence, but this can be explained by their high ionization potentials (10.51 and 9.73 eV, respectively). Although fragmentation of ionized C₅H₁₁⁺ to form C₂H₅⁺ or C₃H₇⁺ is energetically feasible with 9.68-eV photoionization ($\Delta H_{r,xn} = 9.26$ and 9.11 eV, respectively), this is close enough to the photoionization energies used that strong wavelength dependencies would be expected. All of these results are consistent with neutral secondary fragmentation of C₅H₁₁[•], although ionization followed by fragmentation of a highly energetic C₅H₁₁[•] photoproduct cannot be completely ruled out.

Both C₂H₃⁺ and C₃H₃⁺ in the PDPI/MS of 1-octene are probably formed by loss of H₂ following ionization of C₂H₅⁺ and C₃H₅⁺. Both C₂H₃⁺ and C₃H₃⁺ have low ionization potentials (8.9 and 8.7 eV, respectively) but are strongly wavelength dependent. This suggests that C₂H₃⁺ and C₃H₃⁺ are formed by secondary fragmentation after the photoionization step. This ionic fragmentation requires 10.44 eV for formation of C₂H₃⁺ and 10.52 eV for formation of C₃H₃⁺. The low abundance of C₂H₃⁺ and C₃H₃⁺ observed with 9.68-eV photoionization indicates either that some neutral secondary fragmentation takes place ($\Delta H_{r,xn} = 530$ kJ/mol for C₂H₃ and 476 kJ/mol for C₃H₃ formation from 1-octene) or that some of the radicals formed have sufficient excess internal energy to fragment after ionization. The C₂H₃⁺

observed with 9.68-eV photoionization could also be the result of α -cleavage, as discussed previously.

Loss of H_2 is also seen in the secondary fragmentation of 2-alkenes to form $C_4H_5^+$. Unlike the H_2 loss fragments discussed for 1-alkenes, fragmentation of $C_4H_7^+$ during photoionization to form $C_4H_5^+$ requires only 9.0 eV and could occur with 9.68-eV photoionization. Because the ionization potential of C_4H_5 is only 7.95 eV, but the relative abundance of $C_4H_5^+$ is strongly wavelength dependent, H_2 loss probably occurs during the photoionization step.

The high abundance of $C_4H_6^+$ observed in the PDPI/MS of 2-alkenes is unusual because the loss of H^+ is normally very energetic. Formation of $C_4H_6^+$ by ionization and then fragmentation of C_4H_7 requires 10.47 eV, but the ionization potential of C_4H_6 is only 9.07 eV. The high abundance of $C_4H_6^+$ with 9.68-eV photoionization suggests that it is formed as an intact neutral, although ionization and then fragmentation of a highly energetic C_4H_7 photoproduct cannot be ruled out. If the C_4H_6 product contains a conjugated double bond (e.g., 1,3-butadiene) β -cleavage to form C_4H_7 followed by the loss of H^+ to form C_4H_6 is energetically feasible with 193-nm photodissociation ($\Delta H_{rxn} = 498$ kJ/mol). The abundance of $C_4H_6^+$ relative to the abundance of $C_4H_7^+$ decreases with increasing chain length, as would be expected for a secondary neutral fragmentation process.

The 3-alkenes have two β -cleavage sites and exhibit several secondary processes. The presence of an intense peak for $C_3H_5^+$ may be the result of a rearrangement process. The precursor is most likely C_3H_5 because the ion yield is similar at each photoionization energy. One possible mechanism for the formation of C_3H_5 is the loss of C_2H_4 from C_5H_9 via a 1,3-hydrogen shift after β -cleavage at C_5-C_6 ($\Delta H_{rxn} = 412$ kJ/mol). The other product of this reaction (C_2H_4) has an ionization potential of 10.49 eV and is only observed with 10.49-eV photoionization. For alkenes larger than 3-hexene, loss of H_2 from the saturated radical produced by α - or β -cleavage may contribute to the signal for $C_3H_5^+$; however, the abundance observed for 3-alkenes is higher than would be expected for secondary fragmentation of just the saturated radical. The formation of C_3H_5 is not observed in the high-pressure photolysis of 3-hexene [16].

The energetics and apparent yield of C_3H_5 and the other three predominant fragmentation products (C_5H_9 , C_4H_7 , and C_4H_6) are expressed as a percent of the sum of these four fragments in Table 5. The first β -cleavage to form C_5H_9 requires approximately 300 kJ/mol; α -cleavage to form C_4H_7 requires approximately 410 kJ/mol; secondary neutral formation of C_3H_5 after β -cleavage requires approximately 410 kJ/mol; and two successive β -cleavages to form C_4H_6 require approximately 450 kJ/mol. These values are not dependent on the alkyl chain length, and the relative abundances of the ions yield information about the total amount of energy consumed during photodis-

sociation. As the alkyl chain length increases, the abundances of the lower energy fragments ($C_5H_9^+$ and $C_3H_5^+$) increase relative to the abundance of the higher energy secondary fragment ($C_4H_6^+$). This shows that as the alkyl chain length increases, the amount of energy "available" for fragmentation decreases. Molecular size dependencies of this type are well known in mass spectrometry [14, 15]. The abundance of $C_5H_9^+$ relative to $C_4H_6^+$ in the PDPI/MS spectrum of 3-hexene (0.02) is much smaller than that observed with high-pressure photolysis (1.1) [16]. Evidently, the secondary fragmentation in PDPI/MS is more extensive than in a high-pressure photolysis cell.

Qualitative information about the excess energy present in the neutral photodissociation products is available from the amount of ionic secondary fragmentation. Ionic formation of $C_2H_3^+$ from C_2H_5 and $C_3H_3^+$ from C_3H_5 requires 10.44 and 10.52 eV, respectively. Because these values are close to the 10.49-eV photoionization energy, the abundances of these fragments are sensitive to the internal energies of the neutral precursors. As the alkyl chain length increases and the excess energy is distributed among more modes, less internal energy is available to the neutral precursors that form $C_2H_3^+$ and $C_3H_3^+$ after ionization. As a result, the abundances of $C_2H_3^+$ and $C_3H_3^+$ decrease with increasing alkyl chain length. The distribution of excess photoionization energy in the internal energy of the products is also seen in the abundance of CH_3^+ observed with 9.68-eV photoionization. Although the ionization potential of CH_3 is 9.8 eV, photodissociation of 3-alkenes and 2-pentene forms CH_3 radicals with sufficient internal energy that they are observed with 9.68-eV photoionization. In both cases, CH_3 is a primary product of the β -cleavage, and there are few modes to disperse the excess energy.

Energetics of Secondary Fragmentation

From the secondary fragmentation observed for 1-octene, the total amount of energy consumed during photodissociation can be bracketed between 400 and 500 kJ/mol. The saturated radical (C_5H_{11}) undergoes complete neutral secondary fragmentation ($\Delta H_{rxn} = 382$ –397 kJ/mol from 1-octene); some C_3H_3 is formed by neutral fragmentation ($\Delta H_{rxn} = 476$ kJ/mol from 1-octene); and only a small amount of C_2H_3 is formed by neutral fragmentation ($\Delta H_{rxn} = 530$ kJ/mol from 1-octene). β -Cleavage followed by loss of H^+ from C_4H_7 to form C_4H_6 ($\Delta H_{rxn} =$ ca. 500 kJ/mol) is readily observed for small 2-alkenes. As the alkyl chain length increases, however, the relative abundance of $C_4H_6^+$ decreases significantly. The fragmentation observed for 3-alkenes also falls into a similar energy range. As the alkyl chain length increases, the amount of C_5H_9 ($\Delta H_{rxn} = 300$ kJ/mol from the alkene) and C_3H_5 ($\Delta H_{rxn} = 410$ kJ/mol from the alkene) increases, whereas the amount of C_4H_6 ($\Delta H_{rxn} = 450$ kJ/mol from the alkene) decreases.

Comparison with Other Experiments

Fura et al. [17] have recently published angle-resolved neutralization-reionization mass spectra (NRMS) of *n*-hexene isomers that can be compared with PDPI/MS fragmentation patterns. The allylic β -cleavage fragments $C_3H_5^+$, $C_4H_7^+$, and $C_5H_9^+$ are present with both methods. Secondary fragmentation in NRMS is less energetic than that observed with PDPI/MS: The abundance of $C_5H_9^+$, a single β -cleavage, is much higher in the NRMS spectrum of 3-hexene than in the PDPI/MS spectrum. When more energetic collisions are studied with angle-resolved NRMS, the abundance of $C_5H_9^+$ decreases and the abundance of $C_4H_7^+$, β -cleavage at both 3-hexene sites, increases. With NRMS, $C_5H_9^+$ is observed for all three hexene isomers, but only 3-hexene forms $C_5H_9^+$ with PDPI/MS. This indicates that isomerization of the *n*-hexene parent molecules may occur before neutralization or after collisional reionization with NRMS.

In charge remote fragmentation, ion dissociation occurs away from the charge site, and the fragmentation is similar to thermal decomposition of neutral species [18]. As a result, there is some similarity to PDPI/MS. In particular, intense sequence fragments are observed at the β C-C position for charge remote fragmentation of unsaturated alkyl chains [19]. There are, however, significant differences between the two techniques. In charge remote fragmentation, sequential cleavage fragments are formed at each bond along the alkyl chain. Although α -, β -, and γ -cleavage are observed with PDPI/MS, the remaining sequence products are absent from the spectra.

Summary

Unimolecular photodissociation at 193 nm can be used to determine the location of the double bond in linear alkenes. The predominant fragmentation pathway is β -cleavage to form an allylic radical. Secondary fragmentation is also observed and decreases with increasing molecular size. The energetics of these secondary reactions indicate that the total amount of energy con-

sumed during the photodissociation process is between 400 and 500 kJ/mol.

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