JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 90, NUMBER 21 OCTOBER 9, 1968

Physical and Inorganic Chemistry

Chemical Ionization Mass Spectrometry. VIII. Alkenes and Alkynes

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Received March 16, 1968

Abstract: The chemical ionization mass spectra of several alkenes and alkynes have been investigated using methane as reactant. The compounds studied comprised six straight-chain 1-monoolefins, eleven branched and internal monoolefins, and fourteen compounds of diverse types (di- and triolefins, monocyclic and bicyclic monoolefins, a cyclic diolefin, and acetylenes). The straight-chain 1-olefins undergo extensive fragmentation to produce the spectra consisting of series of alkyl and alkenyl ions. From the total intensities of these ion types it is concluded that the attack of the reactant ions on the olefin molecules is not random and occurs predominantly at the double bond. The $(MW - 1)^+$ and $(MW - 15)^+$ intensities are largely in accordance with expectations; that is, they parallel the numbers of allylic hydrogens or methyl groups. The $(MW + 1)^+$ intensities are generally appreciably larger for di-, tri-, and cyclic olefins than for monoolefins, but no enhancement is observed in the acetylenes. Ions with m/e values smaller than $(MW - 15)^+$ are observed, but the reactions involved are not known. Evidence is presented for the occurrence of a 1,2-methide shift.

This paper comprises a report on a study of the chemical ionization mass spectrometry of alkenes and alkynes, which has been undertaken as part of a continuing effort to provide information about the characteristics and scope of chemical ionization mass spectrometry and to study the chemistry of gaseous organic ions. A general description of chemical ionization mass spectrometry has been given,[1] and reports have already been given of the chemical ionization mass spectra of esters,[2] paraffins,[3] aromatics,[4] cycloparaffins,[5] C_7H_8 isomers,[6] and reactions of benzene ions.[7] In the present study of olefins methane is used as the reactant gas, and the procedure used to obtain the chemical ionization spectra is identical with that reported previously. Stated briefly, a pressure of 1 torr of CH_4 is maintained in the mass spectrometer ionization chamber, and as a result of electron impact ionization and ion–molecule reactions a mixture of CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ ions is formed. These in turn react with the olefins, which are introduced into the ionization chamber at an estimated pressure of less than 10^{-3} torr. The chemical ionization mass spectra are produced by these reactions.

Experimental Section

The experiments were made using the Esso chemical physics mass spectrometer and techniques as described previously.[1,3] The methane used was Lif-O-Gen research grade, and its pressure in the ionization chamber was maintained at 1.04 ± 0.02 torr. The temperature of the ionization chamber was 185°. Straight-chain 1-olefins and the three cyclohexenes were API standard samples used as obtained. The remaining compounds save one (1,4-cyclohexadiene) were obtained from the Chemical Samples Co., and the purity of these was investigated gas chromatographically. In a small number of cases the samples studied were purified by preparative scale gas chromatography. All spectra except that of 1,3,5-heptatriene were obtained at least in duplicate using separate

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(1) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

(2) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 4337 (1966).

(3) F. H. Field, M. S. B. Munson, and D. A. Becker, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, p 167.

(4) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **89**, 1047 (1967).

(5) F. H. Field and M. S. B. Munson, *ibid.*, **89**, 4272 (1967).

(6) F. H. Field, *ibid.*, **89**, 5328 (1967).

(7) F. H. Field, P. Hamlet, and W. F. Libby, *ibid.*, **89**, 6035 (1967).

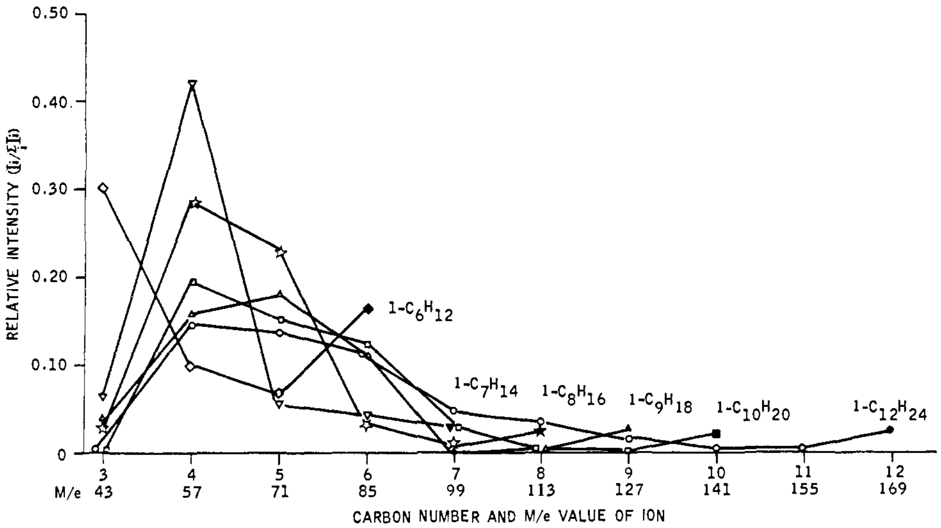

Figure 1. Alkyl ion $(C_nH_{2n+1})^+$ intensities for straight-chain 1-olefins; filled symbols represent $(MW + 1)^+$ ions.

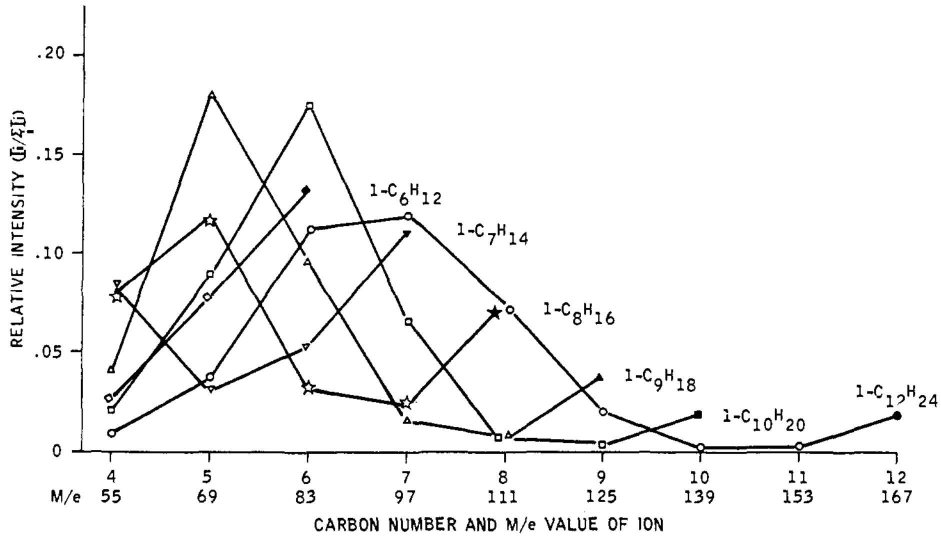

Figure 2. Alkenyl ion $(C_nH_{2n-1})^+$ intensities for straight-chain 1-olefins; filled symbols represent $(MW - 1)^+$ ions.

samples and usually making the runs on different days. The agreement between the replicate runs was quite good.

Results and Discussion

Straight-Chain 1-Olefins. The chemical ionization spectra of six straight-chain 1-olefins from 1-C_6H_{12} to 1-$C_{20}H_{40}$ were determined. The spectra consist almost exclusively of two series of ions, namely, alkyl ($C_nH_{2n+1}^+$) and alkenyl ($C_nH_{2n-1}^+$) ions. To conserve space the intensities of these ions as produced by the several olefins are represented graphically in Figures 1-3. The ordinates are the relative intensities, that is, the ratio of the intensity of the ion with a given *m/e* value to the total intensity of the ions formed from the olefins. The only function of the lines connecting the points in the graphs is that of helping to identify trends in the intensity values. For all of the olefins studied ions with *m/e* = MW (molecular weight) are produced in small but significant amounts, and these values are given in Table I. In addition to these ions, the spectra of all the compounds contain ions at a few (one to five) other mass numbers, but the intensities of these are very small (on the order of a few thousandths of the total ionization), and they will not be considered further here.

The most striking aspect of the straight-chain 1-olefin spectra is that very extensive fragmentation processes occur. As may be seen from Figures 1-3, the intensities of the $(MW \pm 1)^+$ ions decrease from approximately 0.15 to approximately 0.03 as one progresses from 1-C_6H_{12} to 1-$C_{20}H_{40}$. By contrast, in normal paraffins[3] the $(MW - 1)^+$ intensities remain constant at ~0.30 regardless of the size of the molecule, and for cycloparaffins[5] the $(MW - 1)^+$ intensities range between 0.40 and 0.74 for all but one of the compounds investigated. The $(MW + 1)^+$ intensities for cycloalkanes are smaller, ranging from about 0.24 to negligibly small values.

The extensive fragmentation occurring in the alkyl ion series can be explained in terms of the energetics of protonation and alkylation of the double bonds in the molecules. We illustrate in general terms using the group equivalent concept and the group equivalent energies developed by Franklin.[8] Other ion energies are taken from Field and Franklin.[9] The olefins will react

[8] J. L. Franklin, *J. Chem. Phys.*, 21, 2029 (1953).

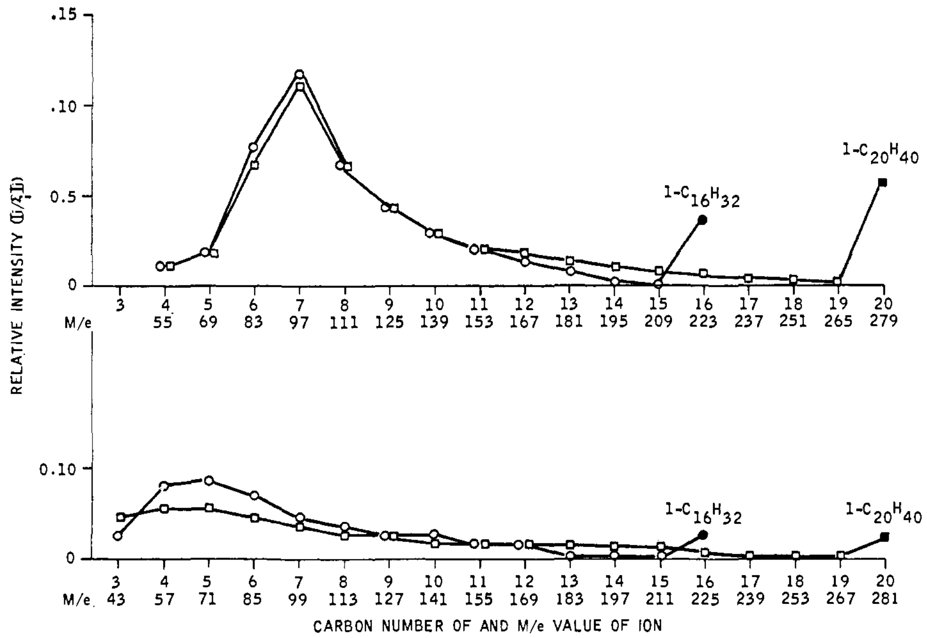

Figure 3. Ion intensities for straight-chain 1-olefins: top, alkenyl ions $(C_nH_{2n-1})^+$, filled symbols represent $(MW - 1).^+$ ions; bottom, alkyl ions $(C_nH_{2n+1})^+$, filled symbols represent $(MW + 1)^+$ ions.

with CH_5^+ and $C_2H_5^+$, which are the main acid species present in the methane plasma, according to reaction 1–3. The heats of reaction are based on ground-state

$$\text{-CH=CH}_2 + \text{CH}_5^+ \longrightarrow \text{-}\overset{+}{\text{C}}\text{HCH}_3 + \text{CH}_4 \quad (\Delta H = -57 \text{ kcal/mol}) \quad (1)$$

$$\text{-CH=CH}_2 + \text{C}_2\text{H}_5^+ \longrightarrow \text{-}\overset{+}{\text{C}}\text{HCH}_3 + \text{C}_2\text{H}_4 \quad (\Delta H = -22 \text{ kcal/mol}) \quad (2)$$

$$\text{-CH=CH}_2 + \text{C}_2\text{H}_5^+ \longrightarrow \text{-}\overset{+}{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_3 \quad (\Delta H = -45 \text{ kcal/mol}) \quad (3)$$

energetics, and thus the negatives of the heats of reaction constitute the maximum excitation energies of the product ions at the moment of their formation. The most likely decomposition reaction of the carbonium ions formed as products in reaction 1–3 is β-fission to produce smaller carbonium ions. Thus

$$\text{-CH}_2\text{CH}_2\underset{\text{H}}{\overset{+}{\text{C}}}\text{-} \longrightarrow \text{-}\overset{+}{\text{C}}\text{H}_2 + \text{CH}_2\text{=CH-} \quad (\Delta H = +45 \text{ kcal/mol}) \quad (4)$$

If rearrangement to produce a secondary carbonium ion occurs, the endothermicity of reaction 4 becomes only 20 kcal/mol. Taking into account the usual uncertainties in the energetics, we conclude that the carbonium ions produced by reactions 1 and 3 have sufficient energy to decompose according to reaction 4, and, if rearrangement to form a secondary ion occurs in reaction 4, the ions formed in reaction 2 can also decompose. Thus it is highly likely that the alkyl ions produced by protonating or ethylating the olefins will decompose to give fragment alkyl ions. However, it is clear from the above calculations that not enough energy is available for multiple β-fission processes, and thus such a sequence of events cannot be invoked to explain the fact that the most intense alkyl ions formed from large olefins contain four to six carbon atoms. Rather we suggest that the alkyl ion initially formed by attack at the double bond undergoes H^- shifts by means of which the charge moves to different positions along the chain, and the observed fragment alkyl ions are produced by β-fission involving the charge at appropriate positions.

Two possible mechanisms for the formation of alkenyl $(C_nH_{2n-1}^+)$ ions exist, namely, a direct mechanism involving abstraction of a hydride or alkide ion from the olefins, or an indirect mechanism involving protonation or alkylation of the olefins followed by loss of H_2. The alkenyl may or may not have the allyl structure. Reactions and energetics for the processes are

$$\text{-CH}_2\text{CH}_2\text{CH=CH}_2 + \text{C}_2\text{H}_5^+ \longrightarrow \text{-CH}_2\overline{\text{CH—CH—CH}_2}^+ + \text{C}_2\text{H}_6 \quad (\Delta H = -42 \text{ kcal/mol}) \quad (5)$$

$$\text{-CH}_2\text{CH}_2\text{CH=CH}_2 + \text{C}_2\text{H}_5^+ \longrightarrow \text{-}\overset{+}{\text{C}}\text{HCH}_2\text{CH=CH}_2 + \text{C}_2\text{H}_6 \quad (\Delta H = -25 \text{ kcal/mol}) \quad (6)$$

$$\text{-CH}_2\text{CH}_2\text{CH=CH}_2 + \text{CH}_5^+ \longrightarrow \text{-CH}_2\overline{\text{CH—CH—CH}_2}^+ + \text{CH}_4 + \text{H}_2 \quad (\Delta H = -44 \text{ kcal/mol}) \quad (7)$$

$$\text{-CH}_2\text{CH}_2\text{CH=CH}_2 + \text{CH}_5^+ \longrightarrow \text{-}\overset{+}{\text{C}}\text{HCH}_2\text{CH=CH}_2 + \text{CH}_4 + \text{H}_2 \quad (\Delta H = -27 \text{ kcal/mol}) \quad (8)$$

Reactions effecting C–C rupture may be written as

$$\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH=CH}_2 + \text{CH}_5^+ \longrightarrow \text{-}\overline{\text{CH—CH—CH}_2}^+ + \text{C}_3\text{H}_6 + \text{H}_2 + \text{CH}_4 \quad (\Delta H = -24 \text{ kcal/mol}) \quad (9)$$

$$\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH=CH}_2 + \text{CH}_5^+ \longrightarrow \text{-CH}_2\text{CH}_3 + {}^+\text{CH}_2\text{CH}_2\text{CH=CH}_2 + \text{CH}_4 \quad (\Delta H = -22 \text{ kcal/mol}) \quad (10)$$

Fragment alkenyl ions are produced by reactions 9 and 10, and reactions such as these can be written for the formation of alkenyl ions with different *m/e* values from a given olefin. Reactions 5–10 are all strongly exothermic, and no decision as to the reactions actually oc-

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(9) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957.

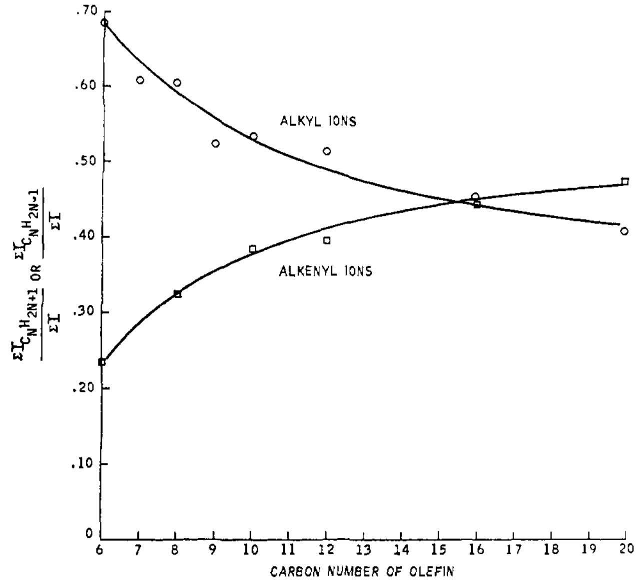

Figure 4. Total alkyl and alkenyl ion intensities from straight-chain 1-olefins.

Table I. Molecule Ion MW$^+$ Intensities

Compound[b]	*m/e*	Intensity[a]
	Monoolefins	
1-C_6H_{12}	84	0.018
3,3-$Me_2C_4^{=}$-1	84	0.027
2,3-$Me_2C_4^{=}$-2	84	0.038
1-C_7H_{14}	98	0.014
2-$MeC_6^{=}$-1	98	0.003
5-$MeC_6^{=}$-1	98	0.003
1-C_8H_{16}	112	0.008
1-C_9H_{18}	126	0.008
2-$MeC_8^{=}$-3	126	0.012
2,2-$Me_2C_7^{=}$-2	126	0.011
2,3-$Me_2C_7^{=}$-2	126	0.030
3,5,5-$Me_3C_6^{=}$-1	126	0.001
1-$C_{10}H_{20}$	140	0.007
cis-2-$C_{10}H_{20}$	140	0.011
trans-2-$C_{10}H_{20}$	140	0.010
trans-4-$C_{10}H_{20}$	140	0.012
1-$C_{12}H_{24}$	168	0.005
1-$C_{16}H_{32}$	224	0.005
1-$C_{20}H_{40}$	280	0.004
	Di, Tri-, and Cyclic Olefins	
1,3-$C_6^{==}$	82	0.028
1,4-$C_6^{==}$	82	0.027
1-$C_6^{\equiv}$	82	0.002
c-$C_6^{=}$	82	0.038
2,4-$Me_2C_5^{==}$-1,3	96	0.038
3-Me-*c*-$C_6^{=}$	96	0.032
1,4-$C_8^{==}$	110	0.010
1,7-$C_8^{==}$	110	~0
1-$C_8^{\equiv}$	110	~0
3-Et-*c*-$C_6^{=}$	110	0.044
1,2-Me_2-*c*-$C_6^{=}$	110	0.095
1,4-*c*-$C_6^{==}$	80	0.062
1,3,5-$C_7^{===}$	94	0.029
Bicyclo[2.2.2]$C_8^{=}$	108	0.009

[a] Corrected for ^{13}C contributions from (MW − 1)$^+$ ions. [b] The superscripts $^{=}$, $^{==}$, and $^{\equiv}$, in this table and throughout the article, refer to one double bond, two double bonds, and one triple bond, respectively.

curring can be made. However, the exothermicities in reaction 9 and 10 enable one to understand the large intensities of fragment alkenyl ions that are observed in the spectra.

For paraffins,[3] cycloparaffins,[5] and aromatics[4] we have suggested that the attack of the reactant ions upon the additive molecules occurs essentially randomly over the structures of the molecule. The results obtained in the present study indicate that in the chemical ionization of olefins the attack is not random. In Figure 4 we plot the sum of the intensities of all the $C_nH_{2n+1}^+$ ions and the sum of the intensities of all the $C_nH_{2n-1}^+$ ions formed from each of the straight-chain 1-olefins studied. In our study of paraffins we found that only alkyl ions were formed, and the reaction involved consisted of either hydride- or alkide-ion abstraction processes. It is reasonable to think that attack of the reactant ions upon the alkyl portion of the olefin molecule will also involve hydride-ion or alkide-ion abstraction reactions, which, however, in this case will produce alkenyl($C_nH_{2n-1}^+$) ions. On the other hand, alkyl ($C_nH_{2n+1}^+$) ions can be formed from the olefins only by proton addition to the olefin molecules, and it is most reasonable to think that this addition occurs at the double bond. We suggest that the sum of the intensities of the alkenyl ions formed from a given olefin serves as a measure of the attack of the reactant ions on the alkyl portion of the molecule and the sum of the intensities of the alkyl ions serves as a measure of the attack at the double bond. Actually, since some attack at the double bond can produce alkenyl ions according to reactions 7 and 9, the alkyl ion intensity serves as a lower limit to the extent of the attack at the double bond.

Referring now to Figure 4 it may be seen that for the smaller olefins attack at the double bond predominates, but as the size of the alkyl group becomes larger an increasing amount of attack along the side chain occurs. This trend is quite reasonable, but we think that the magnitude of the effect of the double bond is of interest. Thus in 1-hexadecene (1-$C_{16}H_{34}$) the attack on the double bond is equal to that on the alkyl group in spite of the fact that the vinyl group contains only 12.5% of the total number of carbon atoms. In previous work we found that the chemical ionization spectra for decanol[1] and for a number of esters[2] indicated that the attack of the reactant ions was occurring at the polar group in these molecules (either the hydroxyl or carbalkoxy groups). Similar results have been obtained with unpublished studies on other polar molecules. Moran and Hamill[10] have shown that the presence of a permanent dipole in a molecule markedly increases the cross section for ion–molecule reaction, and it is quite reasonable to think that the attacking ions in the chemical ionization of polar molecules will be strongly attracted to the polar groups in the molecule. According to McClellan[11] the dipole moment values for straight-chain 1-olefins are in the range of 0.3–0.4 D, and we conclude from our results that a dipole moment of even this small magnitude is sufficient to direct a significant amount of the ionic attack to the double bond in a molecule as large as 1-eicosene.

The field strength in the ionization chamber of the mass spectrometer is 12.5 V/cm, but at 1 torr pressure in the ionization chamber the reactant ions undergo 25–50 collisions before passing out of the ionization chamber. These collisions will limit the amount of

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(10) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, 39, 1413 (1963).

(11) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

Table II. Branched and Internal Monoolefins

Compound	MW	Relative ion intensities[a]															
		C_3	C_4		C_5		C_6		C_7		C_8		C_9		C_{10}		
		m/e 43	m/e 55	m/e 57	m/e 69	m/e 71	m/e 83	m/e 85	m/e 97	m/e 99	m/e 111	m/e 113	m/e 125	m/e 127	m/e 139	m/e 141	$\Sigma C_nH_{2n+1}^+$	$\Sigma C_nH_{2n-1}^+$
3,3-$Me_2C_4^=$-1	84	0.309	0.010	0.141	0.178	0.044	0.059	0.182									0.676	0.247
2,3-$Me_2C_4^=$-2	84	0.236	0.004	0.121	0.024	0.013	0.337	0.174									0.544	0.365
2-$MeC_6^=$-1	98	0.048	0.046	0.445	0.022	0.058	0.056	0.036	0.110	0.077							0.664	0.234
5-$MeC_6^=$-1	98	0.069	0.040	0.436	0.012	0.061	0.118	0.031	0.098	0.043							0.640	0.268
2-$MeC_8^=$-3	126	0	0.018	0.163	0.140	0.167	0.082	0.105	0.017	0.010	0.070	0.004	0.095	0.040			0.489	0.422
2,2-$Me_2C_7^=$-3	126	0.003	0.010	0.229	0.089	0.190	0.046	0.083	0.029	0.006	0.109	0.002	0.097	0.028			0.541	0.380
2,3-$Me_2C_7^=$-2	126	0.001	0.007	0.152	0.065	0.182	0.172	0.076	0.022	0.011	0.021	0.001	0.151	0.039			0.462	0.438
3,5,5-$Me_3C_6^=$-1	126	0	0.013	0.449	0.084	0.189	0.021	0.025	0.005	0.006	0.107	0.002	0.015	0.003			0.674	0.245
cis-2-$C_{10}^=$	140	0.002	0.032	0.177	0.098	0.136	0.163	0.116	0.067	0.035	0.010	0.006	0.005	0.003	0.031	0.031	0.506	0.406
trans-2-$C_{10}^=$	140	0.003	0.035	0.161	0.097	0.120	0.174	0.117	0.068	0.034	0.010	0.005	0.004	0.003	0.053	0.031	0.474	0.451
trans-4-$C_{10}^=$	140	0.005	0.014	0.163	0.095	0.120	0.168	0.108	0.058	0.036	0.023	0.006	0.009	0.003	0.072	0.036	0.485	0.434

[a] At the designated carbon atom and *m/e* values.

kinetic energy the reactant ions will gain from the field, and we estimate that the maximum energy of the reactant ions is 0.1–0.2 eV. For these low energies the ion–molecule reactions comprising the chemical ionization attack on the olefins will proceed *via* the collision complex mechanism,[12,13] and one guesses that in the course of the lengthy, spiralling collision a small dipole moment can exert a considerable effect on the point of attack of the reactant ion.

The values for the MW^+ intensities for the straight-chain 1-olefins decreases steadily from a value of 0.018 in 1-C_6H_{12} to a value of 0.004 in 1-$C_{20}H_{40}$. The ionization potential of 1-C_6H_{12} is 9.45 eV,[14] and the ionization potentials of 1-olefins decrease very slowly as the chain length increases.[15] Ethylene ion ($C_2H_4^+$) is present in the methane plasma to the extent of a few per cent, and the chemical ionization olefin molecule ions are produced primarily by charge exchange with this ion (ionization potential of ethylene is 10.50 eV[16]). The diminution in the MW^+ intensity which occurs between 1-C_6H_{12} and 1-$C_{20}H_{40}$ may be the result of fragmentation of some of the molecule ions produced by the charge-exchange process. Such a possibility is analogous with the known[17] behavior of straight-chain 1-olefins under electron impact, wherein the relative intensities (fraction of total ionization) diminish from 0.043 in 1-C_6H_{12} to 0.0025 in 1-$C_{16}H_{34}$.

Branched-Chain and Internal Monoolefins. We give in Table II the relative intensities of the alkyl and alkenyl ions formed from branched and internal monoolefins. In addition we give for each olefin the sum of the alkyl ions formed and the sum of the alkenyl ions formed. In Table II, as in all of the data given in this paper, C^{13} isotope contributions are not included in ion intensities, although they are included in calculating the total ionization. Thus the intensities of the tabulated ions for any given compound do not sum to unity.

For ease of inspection we give in Table III the relative intensities of selected ions for all of the C_6–C_{10} monoolefins studied. The ions tabulated are $(MW + 1)^+$, $(MW - 1)^+$, and $(MW - 15)^+$.

Table III. Selected Ion Intensities in C_6–C_{10} Monoolefins

Compound	Relative intensity $(MW + 1)^+$	$(MW - 1)^+$	$(MW - 15)^+$
	C_6		
1-C_6H_{12}	0.164	0.132	0.077
3,3-$Me_2C_4^=$-1	0.182	0.059	0.178
2,3-$Me_2C_4^=$-2	0.174	0.337	0.024
	C_7		
1-C_7H_{14}	0.030	0.110	0.053
2-$MeC_6^=$-1	0.077	0.110	0.056
5-$MeC_6^=$-1	0.043	0.098	0.118
	C_9		
1-C_9H_{18}	0.023	0.039	0.009
2-$MeC_8^=$-3	0.040	0.095	0.070
2,2-$Me_2C_7^=$-3	0.028	0.097	0.109
2,3-$Me_2C_7^=$-2	0.039	0.151	0.021
3,5,5-$Me_3C_6^=$-1	0.003	0.015	0.107
	C_{10}		
1-$C_{10}H_{20}$	0.020	0.018	0.002
cis-2-$C_{10}H_{20}$	0.031	0.031	0.005
trans-2-$C_{10}H_{20}$	0.031	0.053	0.004
trans-4-$C_{10}H_{20}$	0.036	0.072	0.009

$(MW + 1)^+$ Ions. The intensities of these ions are greatest for the C_6 olefins and exhibit a rather precipitous diminution in proceeding to the larger olefins, but within the olefins at any given carbon number no marked dependence of the $(MW + 1)^+$ intensity upon structure of the olefin exists. An exception to this behavior is to be found in 3,5,5-$Me_3C_6^=$-1, for which the intensity is only 0.003. Extensive fragmentation is to be observed in this highly branched compound, which is in keeping with the behavior of highly branched paraffins and naphthenes, and the extensive fragmentation reduces the intensity of $(MW + 1)^+$.

MW^+ Ions. When one compares the intensities for the branched or internal olefins with a given carbon

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(12) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

(13) J. H. Futrell and F. P. Abramson, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, p 107.

(14) B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

(15) R. E. Honig, *ibid.*, **16**, 105 (1948).

(16) R. Botter, V. H. Dibeler, J. A. Walker, and H. M. Rosenstock, *ibid.*, **45**, 1298 (1966).

(17) API Project 44, "Tables of Mass Spectral Data," Texas A & M University, College Station, Texas.

number with the intensity for the corresponding straight-chain 1-olefin, one finds that the substitution of alkyl groups at the double bond increases the intensity, and branching away from the double bond decreases the intensity. Thus tetrasubstitution as in 2,3-$Me_2C_4^{=}$-2 and 2,3-$Me_2C_7^{=}$-2 give intensities in the range 0.03–0.04, and disubstitution as in 2-$C_{10}H_{20}$ give values around 0.01. This trend reflects the effect of alkyl substitution on the ionization potential of olefins, and the lower the ionization potential the more likely is charge exchange producing MW^+.

$(MW - 1)^+$ Ions. From Table III and Figure 2 it may be seen that the $(MW - 1)^+$ intensities show a dependence upon the size of the olefin molecule, but in addition some dependence on molecular structure is to be observed. Tetraalkyl substitutions at the double bond has the greatest effect, for the $(MW - 1)^+$ intensities for 2,3-$Me_2C_4^{=}$-2 and 2,3-$Me_2C_7^{=}$-2 are 0.337 and 0.151, respectively. These high values result presumably from the large numbers of allylic hydrogen atoms in these molecules, which are relatively easy to remove.

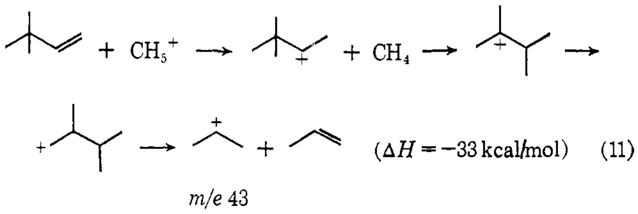
The $(MW - 1)^+$ intensities also are somewhat enhanced by the substitution of only two alkyl groups at the double bond. Perhaps the most interesting behavior is to be observed in the decenes, for which it may be seen in Table III that the $(MW - 1)^+$ intensities increase monotonically in the sequence 1-$C_{10}H_{20}$, *cis*-2-$C_{10}H_{20}$, *trans*-2-$C_{10}H_{20}$, and *trans*-4-$C_{10}H_{20}$. While the intensity differences are small, they are the averages of closely concordant replicate determinations, and we think the differences are experimentally meaningful. The difference between 1-$C_{10}H_{20}$ and the *cis*- and *trans*-2-$C_{10}H_{20}$ may be rationalized on the basis of the degree of alkyl substitution of the allyl ions formed, and the difference between 2-$C_{10}H_{20}$ and 4-$C_{10}H_{20}$ it may be rationalized on the basis of the number of ways in which bisubstituted allyl ions may be formed. The difference between the *cis*- and *trans*-2-$C_{10}H_{20}$ is interesting, but we cannot explain it. The internal C_9 olefins also show an enhanced $(MW - 1)^+$ intensity, and the enhancement is perhaps even somewhat greater than one would have anticipated *a priori* from their structure. The enhanced intensities of the internal olefins conceivably might be of some utility in the difficult analytical problem of the determination of the position of the double bond in an olefin.

The final observation to be made concerning $(MW - 1)^+$ intensities is that in the molecule 3,3-$Me_2C_4^{=}$-1 the $(MW - 1)^+$ intensity (0.059) is significant, although smaller than the intensities in the other hexenes. The formation of $(MW - 1)^+$ ions from this molecule requires that a primary hydrogen be abstracted, and the extent to which this occurs for 3,3-$Me_2C_4^{=}$-1 is very similar to the extent to which it occurs in di-*t*-butylbenzene (0.053).[4] Clearly, the previously made assumption that primary hydrogens are not abstracted[3] is not strictly valid.

$(MW - 15)^+$ Ions. The intensities of these ions show a considerable amount of correlation with structure within a group of compounds containing the same numbers of carbon atoms. The correlations follow established chemical principles. Thus the $(MW - 15)^+$ intensity in 3,3-$Me_2C_4^{=}$-1 is large because a substituted allyl ion is formed, but the intensity in 2,3-$Me_2C_4^{=}$-2 is small because a vinylenic ion is formed. In the C_7 group the intensity in 5-$MeC_6^{=}$-1 is twice that in 2-$MeC_6^{=}$-1 because it has methyl branches other than vinylic branches. Identical arguments apply to the $(MW - 15)^+$ intensities given in Table III for the C_9 olefins.

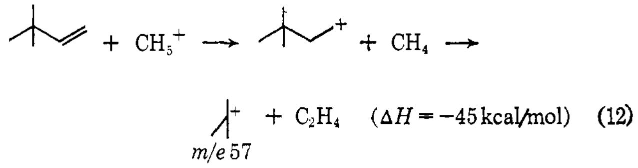
Smaller Fragment Ions. In both the straight-chain and the branched monoolefins extensive amounts of fragmentation to produce ions smaller than $(MW - 15)^+$ occurs, but with the information presently available we are for the most part unable to write the reactions producing the ions.

Limited though our comments must be, we do wish to point out the high intensity (0.309) observed at *m/e* 43 in 3,3-$Me_2C_4^{=}$-1. We suggest that reaction 11



occurs. Reaction 11 requires a 1,2-methide shift, and the formation of $C_3H_7^+$ ions from 3,3-$Me_2C_4^{=}$-1 with $C_2H_5^+$ as reactant would also require a methide shift. Thus the formation of *m/e* 43 from this compound constitutes fairly definite evidence that such methide shifts occur in the gas phase.

The *m/e* 43 ion is the largest in the spectrum in spite of competition from the more exothermic and seemingly simpler reaction 12 producing *m/e* 57 ions.



Di-, Tri-, Cyclic Olefins and Acetylenes. Each of the several compound types investigated produces two series of ions, namely, $C_nH_{2n-1}^+$ and $C_nH_{2n-3}^+$ for C_nH_{2n-2} molecules and $C_nH_{2n-3}^+$ and $C_nH_{2n-5}^+$ for C_nH_{2n-4} molecules. The intensities of the ions in these series are given in Table IV. For ease of comparison the intensities of certain ions are retabulated in a different form in Table V.

$(MW + 1)^+$ Ions. The presence of multiple double bonds or of a ring structure in a molecule increases the intensity of the $(MW + 1)^+$ ion appreciably over that observed in an acyclic monoolefin. A comparison of the $(MW + 1)^+$ columns in Tables III and V yields many examples. The $(MW + 1)^+$ intensities for 1,3,5-heptatriene and 1,4-cyclohexadiene (0.553 and 0.593, respectively) are comparable with the values found in aromatics.[4] Indeed, the affinities of these molecules for added ions are such that their spectra exhibit $(MW + 29)^+$ and $(MW + 41)^+$ ions, which result from the addition of $C_2H_5^+$ and $C_3H_5^+$ ions. By contrast, the presence of a triple bond in the molecule has no perceptible stabilizing effect upon the $(MW + 1)^+$ ion.

The protonation or alkylation of a diolefin by the ions present in the methane plasma are strongly exothermic processes. Thus

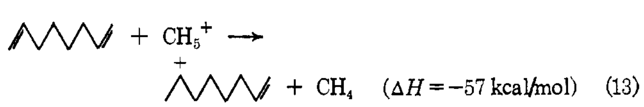
Table IV. Di-, Tri-, and Cyclic Olefins and Acetylenes

		Relative ion intensities[a]											
		C_4		C_5		C_6		C_7		C_8			
Compound	MW	*m/e* 53	*m/e* 55	*m/e* 67	*m/e* 69	*m/e* 81	*m/e* 83	*m/e* 95	*m/e* 97	*m/e* 109	*m/e* 111	$\Sigma C_nH_{2n-1}^+$	$\Sigma C_nH_{2n-3}^+$
1,3-$C_6^{==}$	82		0.318	0.051	0.131	0.074	0.300					0.749	0.125
1,4-$C_6^{==}$	82	0.001	0.430	0.023	0.077	0.108	0.237					0.749	0.132
1-$C_6^{\equiv}$	82	0.006	0.427	0.073	0.096	0.089	0.134					0.657	0.182
c-$C_6^{\equiv}$	82	0.006	0.110	0.030	0.080	0.278	0.357					0.547	0.314
2,4-$Me_2C_5^{==}$-1,3	96	0	0.130	0	0.130	0.028	0.069	0.092	0.390			0.719	0.120
3-Me-*c*-$C_6^{=}$	96	0	0.141	0.008	0.063	0.090	0.040	0.276	0.242			0.486	0.374
1,4-$C_8^{==}$	110	0	0.167	0.045	0.341	0.030	0.063	0.045	0.028	0.092	0.054	0.653	0.212
1,7-$C_8^{==}$	110	0	0.195	0.045	0.417	0.014	0.074	0.013	0.027	0.050	0.040	0.753	0.122
1-$C_8^{\equiv}$	110	0.002	0.204	0.051	0.329	0.038	0.052	0.041	0.017	0.066	0.011	0.744	0.132
1-Et-*c*-$C_6^{=}$	110	0	0.031	0.015	0.156	0.026	0.033	0.046	0.023	0.342	0.159	0.402	0.429
1,2-Me_2-*c*-$C_6^{=}$	110	0	0.016	0.007	0.103	0.013	0.027	0.021	0.007	0.404	0.137	0.290	0.445
		m/e 51	*m/e* 53	*m/e* 65	*m/e* 67	*m/e* 79	*m/e* 81	*m/e* 93	*m/e* 95	*m/e* 107	*m/e* 109	$\Sigma C_nH_{2n-3}^+$	$\Sigma C_nH_{2n-5}^+$
c-1,4-$C_6^{==}$	80	0	0	0	0.103	0.096	0.593				0.020	0.716	0.096
1,3,5-$C_7^{===}$	94	0	0	0	0.049	0.028	0.099	0.074	0.553			0.741	0.102
Bicyclo[2.2.2]$C_8^{=}$	108	0	0	0	0.178	0.050	0.047	0.002	0.033	0.182	0.359	0.617	0.234

[a] At the designated carbon atom and *m/e* values.

Table V. Selected Ion Intensities in Di-, Tri-, and Cyclic Olefins and in Acetylenes

Compound	(MW + 1)$^+$	(MW − 1)$^+$	(MW − 13)$^+$	(MW −15)$^+$
	C_6			
1,3-$C_6^{==}$	0.300	0.074	0.131	0.051
1,4-$C_6^{==}$	0.237	0.108	0.077	0.023
1-$C_6^{\equiv}$	0.134	0.089	0.096	0.073
c-$C_6^{=}$	0.357	0.278	0.080	0.030
c-1,4-$C_6^{==}$	0.593	0.096	0.103	0
	C_7			
2,4-$Me_2C_5^{==}$-1,3	0.390	0.092	0.069	0.028
1,3,5-$C_7^{===}$	0.553	0.074	0.099	0.028
3-Me-*c*-$C_6^{=}$	0.242	0.276	0.040	0.090
	C_8			
1,4-$C_8^{==}$	0.054	0.092	0.028	0.045
1,7-$C_8^{==}$	0.040	0.050	0.027	0.013
1-$C_8^{\equiv}$	0.011	0.066	0.017	0.041
1-Et-*c*-$C_6^{=}$	0.159	0.342	0.023	0.046
1,2-Me_2-*c*-$C_6^{=}$	0.137	0.404	0.007	0.021
Bicyclo[2.2.2]$C_8^{=}$	0.359	0.182	0.033	0.002


$+\ CH_5^+ \longrightarrow$ $+\ CH_4$ $(\Delta H = -57\ \text{kcal/mol})$ (13)


$+\ C_2H_5 \longrightarrow$ $(\Delta H = -66\ \text{kcal/mol})$ (14)

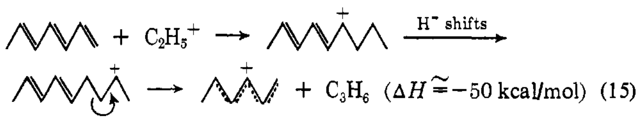
The exothermicities given in reactions 13 and 14 are based on ground-state energetics, and thus the negatives of the exothermicities correspond to the maximum amount of excitation of the ions at the moment of their formation. The exothermicity for a cyclic olefin will be about the same as that of reaction 11. The addition of a proton to a conjugated diolefin would be even more exothermic than reaction 13, and the addition of a proton to 1,3,5-heptatriene would be most exothermic of all.

Our understanding of these variations in the (MW + 1)$^+$ intensities is quite inadequate. The higher intensities to be observed in the cyclic olefins as compared with the acyclic monoolefins (*e.g.*, *c*-$C_6^{=}$ compared with 1-C_6H_{12}) is easily understood as resulting from a smaller tendency of (MW + 1)$^+$ to fragment because of the ring structure. However, the higher intensities in 1,3-$C_6^{==}$ as compared with 1-C_6H_{12} and, more striking, in 2,4-$Me_2C_5^{==}$-1,3 as compared with 1-C_7H_{14} are not so obviously explained.

MW$^+$ Ions. The intensities for these ions follow the ionization potentials of the molecules in the expected fashion. The ionization potentials of the conjugated di- and triolefins are low, and consequently their MW$^+$ intensities are high. The converse is true for the two acetylenes investigated. The equality of the MW$^+$ intensities for 1,3-$C_6^{==}$ and 1,4-$C_6^{==}$ is unexpected.

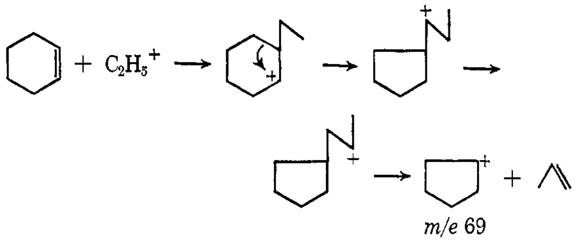
(MW − 1)$^+$. As was the case with the acyclic monoolefins, the (MW − 1)$^+$ intensities for multiple and cyclic olefins correlate with the numbers of allylic hydrogens. Particularly noteworthy are the very high intensities observed in the cyclic olefins, where the combination of allylic hydrogens and the ring structure produce (MW − 1)$^+$ intensities in the range 0.28–0.40 (Table V).

(MW − 13)$^+$ Ions. These ions are not formed in paraffins,[3] cycloparaffins,[5] or aromatics.[4] However, they are formed in moderate abundance in cycloheptatriene and norbornadiene.[6] From Figure 1 and Table II one sees that they are formed with small (0.01–0.04) intensities in C_6 and C_7 monoolefins, and from Table V one sees that they are formed with moderate intensities from a number of the diolefins and the triolefins. The ions may be formed by the loss of CH_2 from the protonated molecule, loss of C from (MW − 1)$^+$, or loss of propylene from the (MW + 29)$^+$ ions. In the study of cycloheptatriene and norbornadiene it was shown that processes involving loss of CH_2 were very unlikely on energetic grounds. Processes involving loss of CH_2 or C from olefins will be at least as unlikely, and the possibility need not be considered further. The simplest mechanism one can write is



$+\ C_2H_5^+ \longrightarrow$ $\longrightarrow$ $+\ C_3H_6$ $(\Delta H \cong -50\ \text{kcal/mol})$ (15)

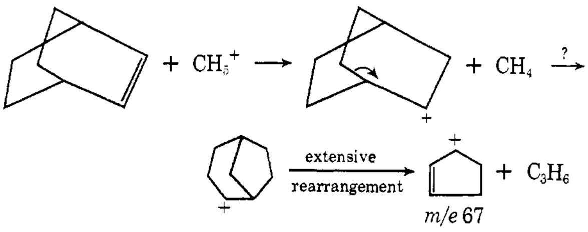
The heat of reaction is obtained from the Franklin group equivalent method,[8] making estimates of the resonance energies involved, and consequently the value given is not very accurate. However, it is accurate enough for one to conclude that reaction 15 is strongly exothermic. Similar mechanisms can be written for the formation of (MW − 13)$^+$ ions from the other compounds. For cyclic compounds it is usually simplest to write reactions retaining the ring structure. Thus



(16)

(MW − 15)$^+$ Ions. The listing given in Table V shows that the intensities of (MW − 15)$^+$ ions correlate closely with the availability of methyl groups, and no further comment is needed.

Smaller Fragment Ions. Comments must be limited, but it is of interest that the *m/e* 67 ion in bicyclo[2.2.2]octene is formed with appreciable intensity (I = 0.178). We found previously[5] that the ion with *m/e* 69 is formed with a similar intensity (I = 0.147) in bicyclo[2.2.2]octane, and, indeed, these two ions are the most intense ions formed by C–C bond rupture in the octene and octane, respectively. This formation of large C_5 ion intensities in these bicyclic compounds leads one to surmise that similar factors are operating in both cases. It is most reasonable to assume that the C_5 ions are cyclic in structure, which requires a skeletal rearrangement. Thus we tentatively write



(17)

The rearrangement to the bicyclo[3.2.1]octyl ion postulated in reaction 17 is supported by the finding of Doering and Farber[18] that the treatment of 2-bromobicyclo[2.2.2]octane with silver bromide in carbon tetrachloride produced the rearrangement product 2-bromobicyclo[3.2.1]octane.

Analytical Considerations. The extensive fragmentation of the larger monoolefins found in this study reduces the utility of the methane reactant chemical ionization technique for the analysis of monoolefins. Clearly the use of a milder reactant such as t-$C_4H_9^+$ as formed from isobutane would give more useful spectra. Comparing the spectra of the monoolefins reported here with the spectra of the monocycloalkanes reported earlier,[5] one sees that the intensities of the $C_nH_{2n-1}^+$ ions are more intense for the cycloparaffins, particularly the (MW − 1)$^+$ ions. This might be of some help in distinguishing between olefins and cycloparaffins in a mixture of the two. However, here also one could anticipate that the use of a mild protonating reagent such as t-$C_4H_9^+$ ions might enable one to ionize preferentially the olefins in the mixture and thus make a much sharper separation of the two compound types.

Acknowledgment. The author thanks Mr. Frank C. Petronis for the experimental measurements reported here and Dr. George M. Kramer for useful discussions.

(18) W. E. Doering and M. Farber, *J. Amer. Chem. Soc.*, **71**, 1514 (1949).