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9. The Chemical Ionization of Organic Compounds

1st Communication

Linear Alkenes with Six to Nine Carbon Atoms

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Summary. The chemical ionization spectra of linear alkenes have been measured using H_2O, CH_4 or CD_3OD as ionizing gas. In the case of 1-heptene the dependence of spectra on pressure, temperature and repeller field strength has been measured and is discussed.

1. Introduction. – The mass spectra of alkenes produced by chemical ionization (CI) with methane as ionizing gas have been described [1]. They are characterized by the formation of the alkenyl ion $(P-1)^+$ by a hydride transfer from the parent olefin $C_nH_{2n}(= P)$. Two homologous series of fragment ions can be observed, the alkyl ions $C_kH_{2k+1}^+$ and the alkenyl ions $C_kH_{2k-1}^+$ $(k < n)$. We have now studied the CI spectra using water or methane as ionizing gas, and have found that in the former an intense alkyl peak $C_nH_{2n+1}^+$ is produced by proton transfer from H_3O^+. This work concentrates on the formation and fragmentation of the heptyl ion formed by protonation of 1-, 2- and 3-heptene, and involves the use of D_2O or CD_4 also as ionizing gases. Hexene, octene and nonene have been studied to a lesser extent. We chose to study the formation of alkyl ions by CI because in this case the upper limit of the ion internal energy can be estimated and is relatively small. This is shown by the small degree of fragmentation observed, when these ions are protonated with H_3O^+, the formation of the butyl ion from heptyl ion being the main reaction.

In two preceeding publications we studied the fragmentation of alkyl ions produced from the corresponding halides by electron impact [2] [3]. We showed that fragmentation must be a rather complex reaction, the loss of an alkene as a neutral fragment by direct scission of a C–C bond being a minor reaction. The probability of losing a terminal carbon atom in the neutral fragment is smaller than or equal to the probabilities of losing one or more of the carbon atoms within the chain. In view of the small energy transferred in the protonation reaction, the rate constants for the fragmentation reaction may be considered as analogous to those observed in the metastable decomposition of the ion produced by electron impact. In forthcoming publications in this series [4] we shall discuss the fragmentation of alkyl ions produced by other ion-molecule reactions and the results obtained after ^{13}C labelling.

2. Experimental. – A single focusing mass spectrometer (*AEI* MS2H) was used, its ion source having been transformed for work at high pressure. Two introduction systems are used in parallel: one at room temperature contains the ionizing gas, the second, which can be heated to 80°, the substance to be investigated; their leaks are situated 20 cm beyond the ion source. The source is made of a single block of stainless steel and is completely closed off from the rest of the mass spectrometer except for an entrance hole for the electrons (∅ = 0.4 mm) and the ion exit slit (0.02 mm × 4 mm). The pressures in the inlet systems and the ion source are measured with membrane manometers (*Barocel* 523). The ion source *Barocel* is connected to the source by a cylindrical tube (∅ 6 mm, length 300 mm). This tube, as well as the gas inlet to the ion source, contains anti-discharge units as described by *Futrell* [5]. The final exit slit of the ion source assembly (0.2 mm × 5 mm) allows differential pumping between the ion source depot and the analyzer. Under normal working conditions the pressure differentials between source, source housing and analyzer are $2 \cdot 10^5 : 10^3 : 1$. Unless otherwise indicated, the pressure conditions in the ion source correspond to 3 mTorr for sample and 250 mTorr for ionizing gas. The source temperature is measured with a Fe-constantan thermocouple in the source block. An additional electrode with a central hole of 0.5 mm diameter between the filament and the source block serves as a heat shield. The initial temperature of the ion source is 60°; when the filament is switched on, it rises by about 1.5°/min to a final temperature of 120°. The gas inlet is behind the repeller plate in order to ensure that the gas attains thermal equilibrium with the ion source.

The ion acceleration voltage is 2 kV, the electron energy is 400 eV. The repeller is at a distance of 5.4 mm from the ion exit slit; its potential corresponds to a field of $8.8\ \mathrm{V \cdot cm^{-1}}$. The electron-beam passes at equal distances from the repeller and the ion exit slit and corresponds to a trap current of 5 μA. The mass spectrometer is coupled 'on-line' to a computer (*Hewlett Packard* 2114A, 8 K memory) which controls the magnetic field. A *Faraday* cup and a vibrating reed amplifier serve as detector; the signal is then transferred to the computer by an A/D converter (13 bit). The program allows for scanning of selected mass ranges in order to gain time (for measurement of temperature dependence) and signal averaging to recover small peaks with increased accuracy, for some measurements a signal averager (*Nicolet* 1074) was used. The products used were of commercial purity and were purified by gas chromatography whenever necessary.

3. Results and discussion. – 3.1. *Ionizing gases.* CH_4, CD_4, H_2O and D_2O resp. were used; in some cases CD_3OD. Their proton affinities (PA) are given in Table 1, where PA_Y is defined as $-\Delta H_f$ of the following reaction:

$$Y + H^+ \longrightarrow YH^+ \tag{1}$$

Table 1. *Proton affinities (PA) of the ionizing gases*

Y	CH_4	C_2H_4[a])	H_2O	CH_3OH
PA in kJ/mol	493	660	685	748
ref.	[6]	[7]	[8]	[9]

[a]) PA(C_2H_4) is given as in methane $C_2H_5^+$ and CH_5^+ ions have comparable intensities.

3.1.1. *Methane.* The mass spectrum of CH_4 in the pressure range used is characterized by high concentrations of CH_5^+ and $C_2H_5^+$ which are formed in the following reaction sequences [10]:

$$CH_4 \xrightarrow{e^-} CH_4^+, CH_3^+ \tag{2}$$

$$CH_4^+ + CH_4 \xrightarrow{k_3} CH_5^+ + CH_3^{\cdot} \tag{3}$$

$$CH_3^+ + CH_4 \xrightarrow{k_4} C_2H_5^+ + H_2 \tag{4}$$

Peaks of $m/e = 41$ and 43 have intensities of about 10% and 1% resp. of the $C_2H_5^+$ ion, and preclude measurement of product ion intensities in the C_3-mass range.

In order to test the system for pressure measurement, we determined k_3; the value found ($k_3 = (8 \pm 1) \cdot 10^{-10}$ cm$^3 \cdot$ molecule^{-1} s^{-1}) agrees well with the average value found in the literature ($12 \cdot 10^{-10}$ cm$^3 \cdot$ molecule^{-1}s^{-1} [11a]). However we observed that at high pressure the methane spectrum is very sensitive to the presence of impurities in the ion source, especially if water has been used previously. In order to obtain reproducible results, we flushed the spectrometer with methane under slight pressure for 48 h before starting measurements with methane as ionizing gas.

3.1.2. *Water.* The CI spectrum with water as ionizing gas shows a smaller degree of fragmentation than that with methane owing to the higher proton affinity of water. Furthermore as we encountered fewer difficulties with impurities, we concentrated on the use of H_2O. A large concentration of hydronium ion is typical for the mass spectrum of water at high pressure:

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH\cdot \qquad (5)$$

This ion is solvated according to the equilibrium

$$H(H_2O)_n^+ + H_2O \rightleftharpoons H(H_2O)_{n+1}^+ \qquad (6)$$

Ions with $1 \leqslant n \leqslant 8$ have been observed [12]. The equilibrium constants

$$K_{n,n+1} = (I_{H(H_2O)_{n+1}^+} / I_{H(H_2O)_n^+}) / P_{H_2O}$$

determined by different authors are given in Table 2. The original data have been standardised for a temp. of 393 K by calculation using the ΔH values given by the authors; especially for $n = 1$ the variation among different authors is very great and not yet explained. We cannot ascertain whether our measurements correspond to equilibrium values; that they correspond best to those of *Field* [13] is not astonishing given the similarity of the experimental conditions. Possible reasons for the large differences between different authors, especially for $K_{1,2}$, have been discussed (see lit. cited in Table 2 and [16]); the main question is whether equilibrium has been attained.

Table 2. *Equilibrium constants for solvation of the proton*

n, n+1	Ke	F	BF1	BF2	this work
1, 2	$1.3 \cdot 10^9$	–	34	300	23
2, 3	$1.6 \cdot 10^3$	10	47	44	8.5
3, 4	2.4	1.8	2.6	2.2	2.7

Ke: *Kebarle et al.* [12]; (0.1 to 1 Torr H_2O; 5 Torr Ar).
F: *Field* [13]; (0.5 Torr H_2O; $E_{rep} = 12.5$ V $\cdot$ cm^{-1}).
BF1: *Beggs & Field* [14]; (0.01 Torr H_2O, 1 Torr CH_4).
BF2: *Beggs & Field* [15]; (0.01 Torr H_2O, 1 Torr C_3H_8).
this work: 0.3 Torr H_2O, $E_{rep} = 2.9$ V $\cdot$ cm^{-1}.

It should be noted however that the values obtained by *Kebarle et al.* [12] were extrapolated from rather high temperatures, especially for $K_{1,2}$ (700 K) and the *van't Hoff* diagram usually shows some curvature. *Beggs & Field* consider that equilibrium conditions are only attained when the concentration of the products is less than 10% of that of the adducts [15]. These requirements are fullfilled even at temperatures below 400 K, but the results of different authors nevertheless differ by orders of magnitude. Most of the systems studied involved other equilibria (CH_4 +

H_2O, $C_3H_8 + H_2O$) together with a secondary compound for increasing the pressure. The result is that either the ions $H(H_2O)_n^+$ represent only a minor fraction of all ions observed (as in the case of propane), or that not even all ions are included (as for methane) (*cf.* Tables 1 of [14] and [17]). Thus the difficulty of determining true equilibrium values with the mass spectrometer is evident. As an illustration of this, we found that by increasing the repeller field to a value of 17 V · cm^{-1}, the concentration of H_3O^+ in the source (120°, 0.3 Torr) increases to over 90% of the total ionization.

3.1.3. *Methanol.* The ion-molecule reactions in methanol have been described [16] [17]. In our case deuteriated methanol was used because the ion $H(CH_3OH)_3^+$ mass 97, would interfere with the measurements of the heptenyl ion. The spectrum of CD_3OD at 0.25 Torr is given in Table 3. One observes the successive solvation of the deuteron, on the other hand a similar series starting with the ion of $m/e = 54$, the latter corresponding probably to a loss of D_2O from the doubly solvated deuteron:

$$D(CD_3OD)_2^+ \longrightarrow (CD_3)_2OD^+ + D_2O \tag{9}$$

Table 3. *The principal ions in the spectrum of deuterated methanol at 0.16 Torr*

m/e	34	38	54	74	90	110
ion	CD_3O^+	$D(CD_3OD)^+$	$D(CD_3)_2OD^+$	$D(CD_3OD)_2^+$	$(CD_3)_2OD^+ \cdot CD_3^+OD$	$D(CD_3OD)_3^+$
$\% I_{tot}$	1	44	6	30	4	15

3.2. *Energetic considerations concerning the formation of alkyl ions.* The influence of the ionizing energy on the formation of heptyl ion is shown in Fig. 1. The degree of fragmentation is largest when methane is used as ionizing agent because the energy transferred is the highest. Heptyl ions formed from *n*-heptyl iodide by electron impact [4] provide an intermediate case, and for water as ionizing agent for 1-heptene only one main reaction can be observed. For comparison purposes the electron-impact spectrum of 1-heptene is given, the only one showing notable amounts of ions with two and four carbon atoms. It is difficult to define the internal energy of the heptyl ion formed by electron impact (70 eV) of the iodide ion; the reaction

$$C_7H_{15}I^{+\cdot} \longrightarrow C_7H_{15}^+ + I - 21\ \text{kJ/mol} \tag{10}$$

is endothermic, but the internal energy of the parent ion is not known. The protonation of an alkene C_nH_{2n} by YH^+ allows the formation of the corresponding alkyl ion with an internal energy which has, as upper limit, the energy of the following reaction:

$$C_nH_{2n} + YH^+ \longrightarrow C_nH_{2n+1}^+ + Y \tag{11}$$

The reaction enthalpy ΔH_r varies according to the structure of the ion formed (Table 4a). These figures are valid for linear 1-alkenes with more than five carbon atoms¹). For non-terminal alkenes, the values are about 8 kJ/mol lower.

By changing the protonating agent the energy of reaction is altered; when using methane as ionizing gas there is additional complication owing to the presence of at

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1) The formation enthalpies of the ions are taken from [7] or calculated by the group method given by *Franklin* [18].

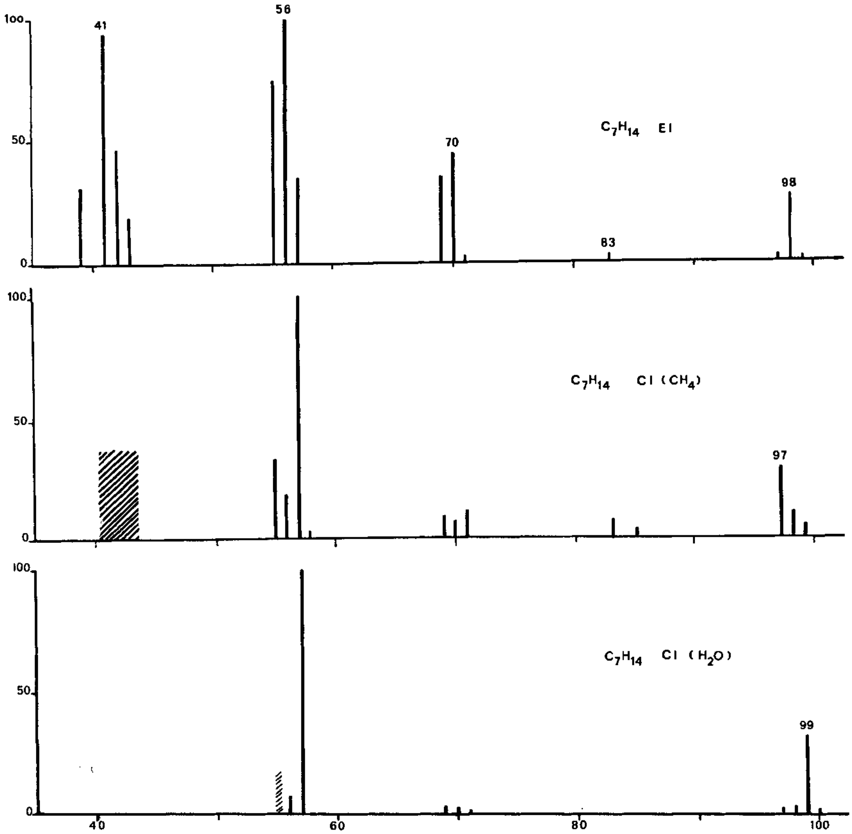

Fig. 1. *Mass spectrum of 1-heptene under different conditions*

Table 4. *Enthalpy values used*

a) *Reaction enthalpy* ΔH_r (kJ/mol) *for rn.* (*11*) ($n > 6$)

$C_nH_{2n+1}^+$	$YH^+ = H_3O^+$	CH_5^+	$C_2H_5^+$
prim.	+ 58	−134	+ 31
sec.	− 46	−238	− 73
tert.	−107	−301	−136

b) *Reaction enthalpy* ΔH_r *for the formation of alkenyl ion by* $C_2H_5^+$, *rn.* (*12*)

$C_nH_{2n-1}^+$	prim.	sec.	tert.
ΔHr (kJ/mol)	− 71	−176	−238

c) ΔH_r *for rn.* (*18*) *as a function of the structure of the reacting ions*

	$C_7H_{15}^+$	$\rightarrow$	$C_4H_9^+$ +	C_3H_6
prim.	836		911	
sec.	732		802	21
tert.	669		736	

least two species, CH_5^+ and $C_2H_5^+$; the latter can effect an abstraction of a hydride ion according to:

$$C_2H_5^+ + C_nH_{2n} \longrightarrow C_nH_{2n-1}^+ + C_3H_6 \qquad (12),$$

where again the reaction enthalpy ΔH_r depends on the structure of the alkenyl ion (Table 4b).

The ion distribution in alkene spectra, using H_2O or CH_4, is classified according to the number of carbon atoms in Table 5. The values show a similarity between the heptyl, octyl and nonyl ions, all of which show approx. 70% fragmentation, heptyl forms mainly butyl, pentyl and hexyl ions. The fragmentation of hexyl ion however is much smaller, mainly protonation to $(P + 1)^+$ is observed in spite of the fact that ΔH_f does not differ from those for the higher alkyl ions.

Table 5. *CI spectra of 1-alkenes with n carbon atoms in ‰ of the total ionization for all ions with more than three carbon atoms*

C_nH_{2n}	C_6H_{12}	C_7H_{14}	C_8H_{16}	C_9H_{18}	C_7H_{14}
ion. gas		H_2O			CH_4
$(P + 1)^+$	720	211	219	314	22
P^+	40	19	16	14	33
$(P - 1)^+$	40	16	15	26	128
C_n	800	246	250	354	183
C_{n-1}	20	9			44
C_{n-2}	82	50	33		125
C_{n-3}	98	666	330	167	646
C_{n-4}		29	300	304	
C_{n-5}			83	175	

P^+: $C_nH^+_{2n}$; $\sum_i C_k$: $C_kH_i^+$; k = n, n − 1.....

3.3. *The parent ion group.* The *alkyl ion* $(P + 1)^+$ is formed by the proton transfer reaction (11). The smaller the energy of reaction the higher is the relative intensity of the $(P + 1)^+$ ion, since its fragmentation reactions are always endothermic. The possibility of forming the *alkene ion* P^+ by electron impact can be excluded because of the very small intensity of the fragment ions resulting from such an impact (see Fig. 1 and Table 5). It was difficult to obtain reproducible values for the P^+ ion when using methane as the ionizing gas, the variation being ±20%. Therefore we studied the effect of varying the partial pressure of methane, between 0.1 and 0.3 Torr, on the fragmentation of heptene. In this pressure range we can distinguish two groups of ions: those of m/e = 99, 97, 71 and 57 are relatively independent of pressure and considered to be the 'pure' CI spectra; those of the parent ion P^+ and its principal fragments (mainly $C_5H_{10}^+$ and $C_4H_8^+$) for which the intensities decrease with pressure. The following charge transfer reaction offers a possible explanation:

$$CH_4^+(IP = 13.1\ eV) + C_nH_{2n} \rightarrow CH_4 + [C_nH_{2n}^+(IP = 9.5\ eV) \rightarrow C_kH_{2k}^+ + C_{n-k}H_{2(n-k)}] \qquad (13)$$

The corresponding measurement of pressure dependence using water as ionizing gas shows that the formation of the alkenyl ion $(P - 1)^+$ probably occurs, at least in part, by loss of H_2 from the alkyl ion, in spite of the fact that this reaction is endothermic by 42 kJ/mol. The larger energy of the protonation reaction in methane is reflected by the higher relative intensity of the alkenyl ion with this ionizing gas as compared to water (Table 5). Reaction (12) with $C_2H_5^+$ might also contribute to the formation of the alkenyl ion. However, no metastable transition $(P+1)^+ \longrightarrow (P-1)^+$ could be observed, suggesting that the protonating ion gives a collision complex which decays directly to the alkenyl ion.

3.4. *Influence of H_2O pressure.* The CI(H_2O) spectrum of 1-heptene was measured as a function of the water pressure. The variation of the relative intensities of the two main ions with different values in the repeller-field E_{rep} is shown in Fig. 2;

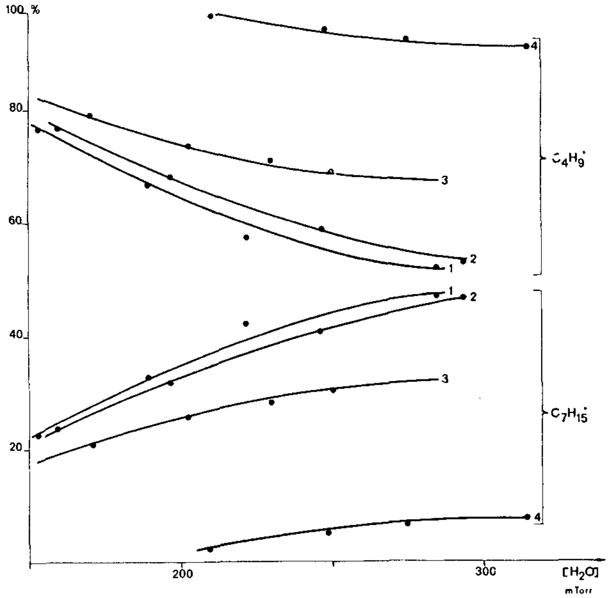

Fig. 2. *Pressure dependence of the relative intensity of the heptyl and butyl ions from 1-heptene as a function of the repeller field.* $E_{rep} = 0(1), 2.9(2), 8.7(3), 17.3(4)\ V \cdot cm^{-1}$

the relative concentration of heptyl ions increases with pressure and decreases with E_{rep}. This behaviour parallels the changes in water spectra (see 3.1.2.), suggesting that the higher solvation states of the proton can also protonate heptene, though without supplying sufficient energy to enable fragmentation of the resulting alkyl ion. Another possibility is a collision-induced fragmentation. The pressure dependence of fragmentation leads us to propose the reaction scheme (14) to (20) for the reaction between H_2O ions and 1-heptene:

$$H_2O^+ + H_2O \longrightarrow H_3O^{+*} + OH\cdot \quad (14)$$

$$H_3O^{+*} + H_2O \longrightarrow H_3O^+ + H_2O \quad (15)$$

$$H_3O^{+*} + C_7H_{14} \longrightarrow C_7H_{15}^{+*} + H_2O \quad (16)$$

$$C_7H_{15}^{+*} + H_2O \longrightarrow C_7H_{15}^+ + H_2O \quad (17)$$

$$C_7H_{15}^{+*} \longrightarrow C_4H_9^+ + C_3H_6 \quad (18)$$

$$H_3O^{+*} + H_2O \longrightarrow H(H_2O)_2^+ \quad (19)$$

$$H(H_2O)_2^+ + C_7H_{14} \longrightarrow C_7H_{15}^+ + 2H_2O \quad (20)$$

With a proton affinity of 685 kJ/mol for H_2O [8], reaction (14) is exothermic by 79 kJ/mol and the H_3O^{+*} will be in an excited state. This ion can either lose its excess energy by successive collisions (15) or protonate heptene by forming an excited heptyl ion (16). *Friedman et al.* have shown that the de-excitation of H_3O^{+*} by H_2O is a slow process [19] and also that the internal energy of H_2O^+ depends upon the electron energy (15–25 eV) used to produce these ions; however in the range 120 to 400 eV we used, the electron energy had no such influence. For H_3O^+ in the ground state reacting to form a secondary or tertiary C_7H_{15}-ion (formed by rearrangement of 1-heptene), reaction (16) is exothermic by 46 kJ/mol and 109 kJ/mol, resp. The resulting C_7H_{15}-ion will therefore possess a fair amount of internal energy. This energy can either be used for an (endothermic) fragmentation (18) or lost by collision with water (17). H_3O^+ is in equilibrium with its solvated species $H(H_2O)_2^+$ (19) which can also protonate heptene (20). An average value for the solvation energy of reaction (14) seems to be about 96 kJ/mol so that the resulting C_7H_{15}-ion will not acquire enough energy for fragmentation [12–14]; this is also the case for protonation by more highly solvated protons. Similar behaviour has been found in the protonation of a tripeptide [20].

We found that for 1-heptene the ratio

$$C_7H_{15}^+ / C_4H_9^+ = -0.10 \pm 0.02 + (2.23 \pm 0.09) [H_2O] \qquad (21)$$

depends linearly upon the H_2O pressure ($[H_2O]$ expressed in Torr); similar values were found for the isomeric heptenes, see Fig. 3. The ratio given in (21) also varies linearly with the repeller field:

$$d(C_7H_{15}^+/C_4H_9^+) / d[H_2O] = 4.8 \pm 0.3 - (0.25 \pm 0.03) \cdot E_{rep} \qquad (22)$$

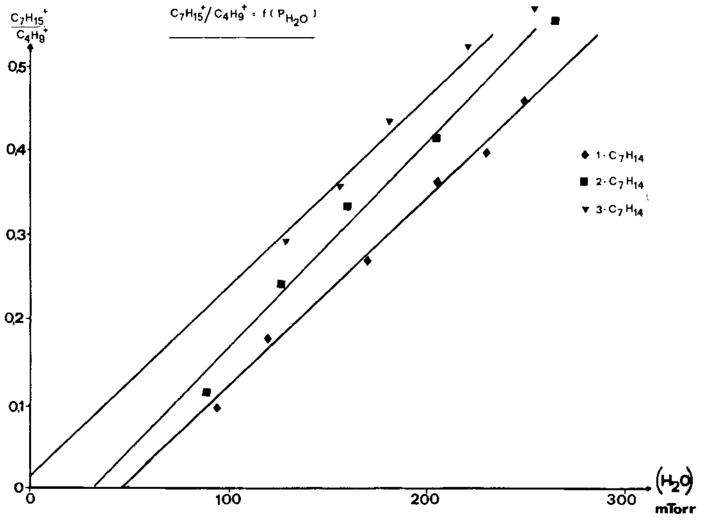

Fig. 3. *Pressure dependence of the ratio of the concentrations of heptyl and butyl ions for different heptenes*

where E_{rep} is expressed in $V \cdot cm^{-1}$ and the water concentration in Torr as shown in Fig. 4.

The kinetic scheme described above involves other complications depending on the ratio of the rate constants k_{15} and k_{17} for de-excitation and the number of collisions needed to take away sufficient energy. From the evidence discussed above we make the assumption that reactions (16) to (20) are the rate determining steps. This gives us the simplified expression

$$C_7H_{15}^+ / C_4H_9^+ = (k_{coll.}/k_{18})\,[H_2O] \tag{23}$$

where $k_{coll.}$ depends upon the collision frequency. The ideal condition for an ion-molecule reaction is the absence of any electric field within the ion source. In view of the construction of the source and the very small exit slit, we approximate this condition to $E_{rep} = 0\ V \cdot cm^{-1}$. The ratio $k_{coll.}/k_{18}$ is then equal to $4.8\ Torr^{-1} = 2 \cdot 10^{-16}$ $cm^3 \cdot molecule^{-1}$. The order of magnitude of $k_{coll.}$ may be taken to be $10^{-9}\ cm^3 \cdot molecule^{-1}s^{-1}$ (assuming that only one collision is needed for deactivation), giving $k_{18} \cong 5 \cdot 10^6\,s^{-1}$, which seems reasonable as order of magnitude.

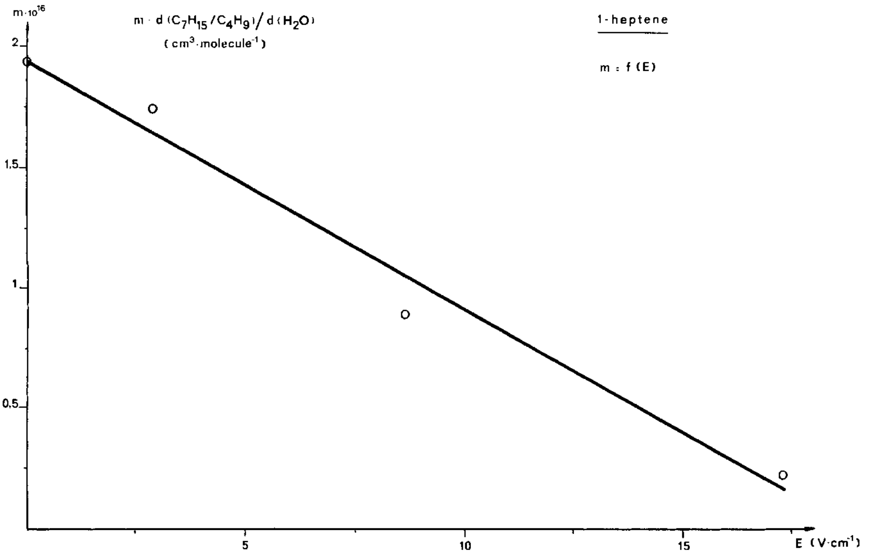

Fig. 4. *Slope of the pressure dependence of the ratio of heptyl to butyl ions in 1-heptene as a function of the repeller field*

3.5. *Temperature dependence.* On the not necessarily justified assumption that reaction (18) proceeds under conditions of thermal equilibrium, the following equations can be derived [11b] [14]:

$$\alpha(\tau) \equiv C_7H_{15}^+ / (C_7H_{15}^+ + C_4H_9^+) = (1 - \exp(-k_{18} \cdot \tau)) / (k_{18} \cdot \tau) \tag{24}$$

where τ is the residence time of $C_7H_{15}^+$ in the ion source. The equation can be solved by successive approximation. α has been measured in the temperature range from 60° to 120°. Our instrument scans the two regions corresponding to fragments with four and seven carbon atoms in 30 s, which corresponds to a systematic temperature difference of about 1° between the time of measurement of the C_4 and the C_7 regions.

Fig. 5 gives the dependence of $\ln(k_{18} \cdot \tau)$ on 1/T for 1-, 2- and 3-heptenes in H_2O, and slope corresponds to an activation energy of $E_a = 17 \pm 2$ kJ/mol for all three isomers; with methane as ionizing gas, $E_a = 12 \pm 2$ kJ/mol. The slight curvature in Fig. 5 might stem from the fact that the (unknown) residence time τ may also vary with temperature.

Ionization in D_2O yields butyl ions corresponding to *m/e* 58 and 59, for which the sum shows the same temperature dependence as with H_2O and the ratio does not change with T. *Field* [11b] interpreted such activation energy E_a as the difference between the ground state of the parent ion and the minimum energy needed for the fragmentation studied, *i.e.* the endothermicity of reaction (18). The values in Table 4c show that the energy needed to form a tertiary butyl ion from a secondary C_7H_{15}-ion is 25 kJ/mol, in reasonable agreement with the measured E_a values cited above. In a similar case, we found an activation energy of 21 ± 2 kJ/mol [4] for C_7H_{15}-ion produced in the CI(H_2O) spectrum of $C_7H_{15}I$.

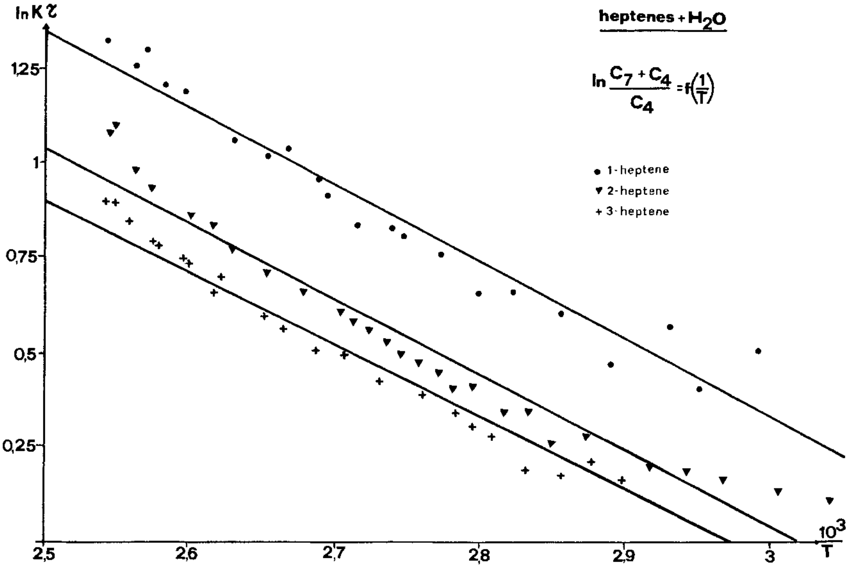

Fig. 5. *Temperature dependence of the expression* $k_{18} \cdot \tau$ *for different heptenes with water as ionizing gas*

3.6. *Fragmentation of the heptyl ion.* The CI mass spectra of the heptenes are given in Table 6 together with their electron impact spectra (EI). Since there is no perceptible difference between the CI spectra of 2- and 3-heptene, the average for their values are given. The main reaction is the loss of C_3H_6 from the protonated heptene giving a butyl ion. This reaction has been studied by electron impact [4], and was shown to be not a simple C–C fragmentation, as in the neutral fragment any carbon atom in the chain has a finite probability of being lost. Fragmentation is less for CI(CH_4) than by electron impact and even less for CI(H_2O), reflecting the progressively smaller energy imparted to the parent ion in CH_4 and H_2O resp. In 1-heptene the proton is very probably attached at the 1-position, and so the exothermicity is about 8 kJ/mol larger than in 2- and 3-heptene, where it is in a secondary position.

This might explain the somewhat higher degree of fragmentation of 1-heptene, especially with water as ionizing gas. With methane an important reaction is the loss of C_3H_6 from the heptenyl ion; the ion at $m/e = 85$ cannot be originated from the heptyl ion, but is evidence for a transition complex e.g. with the ethyl ion, though there was no evidence for an ion at $m/e = 127$.

When a deuteriated ionizing gas such as D_2O or CD_4 is used, one deuteron is transferred in the deuteronating process, and the parent ion can then lose either C_3H_6 (giving $m/e = 58$) or C_3H_5D. The ratio of the two resulting ions is given in Table 7; apparently there is no complete scrambling of the D-atom coupled with a statistical loss. A D-atom in one of the positions 2 to 6 apparently has a larger probability of being lost in a neutral fragment, especially if D_2O is used as ionizing gas. This is confirmed by the metastable transitions at $m/e = 33.7$ and 32.6 with D_2O, yielding a ratio $(100 \rightarrow 58) / (100 \rightarrow 57)$ of 1.8 ± 0.2 for 1-heptene and 1.0 ± 0.2 for 2- and 3-heptene. A similar observation was made for this reaction when induced by electron impact [2].

Table 6. *The mass spectra of heptenes given as percent total ionization of the ions listed*

	1-heptene					mean of (2- + 3-heptenes)					3-heptene	
m/e	EI	H_2O	D_2O	CH_4	CD_4	EI	H_2O	D_2O	CH_4	CD_4	CD_3OD[a]	CH_3OH[b]
39	6	1	[c]	[c]		5			[c]			
41	19	1	[c]			20	1	[c]				
42	9	1				4		[c]				
43	3	1		[c]		4			[c]			
55	15	[c]	5	15	17	18	[c]	4	17	14	19	11
56	19	4	5	8	9	18	4	4	7	6	15	8
57	6	63	22	43	20	2	56	26	38	22	19	38
58			40		18			32		20	25	
69	7	2	1	5	5	14	3	2	7	6		
70	9	2	1	3	5	3	1		2	2		
71		1		5	2		1		4	2		
72					1					3		
83	1			3	3	2			4	4		
85				2	1				2	2		
97	1	2	2	13	11	1	2	2	14	14	3	[c]
98	6	2	2	3	5	11	2	2	4	5	3	
99		21	1	2	1		26	1	2	2	1	43
100			20		2			24			9	
101											6	

[a] 0.16 Torr. [b] 0.20 Torr. [c] this mass contains an important contribution from the ionizing gas.

3.7. *CI* (*CD_3OD*) *spectrum of 3-heptene.* The PA of methanol (748 kJ/mol) is comparable to that for heptene. The exothermicity of the formation of the deuteronating agent

$$CD_3OD^{+\cdot} + CD_3OD \longrightarrow CD_3OD_2^+ + CD_2O\cdot \qquad (25)$$

(67 kJ/mol) is also less than that of water (79 kJ/mol). The C_7H_{15}-ions formed should therefore show even less fragmentation. The mass spectrum at a pressure of 0.16 Torr of CD_3OD is given in Table 3. Although the energy involved in the deuteron transfer

Table 7. *Distribution in % of butyl ions in the CI spectra of heptenes with deuteriated ionizing gases*

ion. gas	*m/e*	1-heptene	2-heptene	3-heptene	stat. distrib.
D_2O	57	36	46	46	40
	58	64	54	54	60
CD_4	57	45	48	50	40
	58	55	52	50	60

clearly must be smaller than with water, the fragmentation is larger, which shows the difficulty of predicting CI mass spectra. We believe that $CD_3OD_2^+$ forms a relatively long-lived complex with heptene, thus allowing some H/D exchange between CD_3OD and heptene ($m/e = 101$). A similar exchange has been observed for the reaction between propyl ion and CD_3OD [21] using an ion cyclotron resonance instrument.

3.8. *CI (H_2O) of 1-nonene.* The CI (H_2O) spectrum of 1-nonene is given below:

m/e:	55	56	57	69	70	71	83	84	85	125	126	127
I_{rel}:	*	3	15	5	4	22	3	2	12	3	1	31

The decomposition of nonyl ion corresponds to the following three reactions:

$$C_9H_{19}^+ \longrightarrow \left\{ \begin{array}{ll} C_6H_{13}^+ + C_3H_6 & (26) \\ C_5H_{11}^+ + C_4H_8 & (27) \\ C_4H_9^+ + C_5H_{10} & (28) \end{array} \right.$$

Furthermore corresponding alkene and alkenyl ions are always formed in non-negligible amounts depending upon the pressure of the ionizing gas, see Table 8. The values a and b are calculated from the following expression:

$$V = a + b\,([H_2O] - 0.25) \qquad (29)$$

where $[H_2O]$ is given in Torr. The ratio $C_9H_{18}^+/\Sigma$ (fragments) can be compared with the corresponding ratio for heptyl ions (see 3.4). The slopes for 1-heptene with $b = 2.23 \pm 0.29$ (eq. 22) and for 1-nonene with $b = 1.7 \pm 0.3$ (Table 8) are nearly

Table 8. *Pressure dependence of the CI (H_2O) spectrum of 1-nonene*

V equ. (29)	a	b [Torr^{-1}]
$C_9H_{19}^+/\Sigma$(fragments)	0.315 ± 0.08	$+1.7 \pm 0.3$
$\Sigma(C_kH_{2k+1}^+)/\Sigma$(fragments) $k < g$	0.72 ± 0.05	$+1.2 \pm 0.1$
$\Sigma(C_kH_k^+)/\Sigma$(fragments) $k < g$	0.13 ± 0.05	-0.6 ± 0.1
$\Sigma(C_kH_{k-1}^+)/\Sigma$(fragments) $k < g$	0.15 ± 0.02	-0.6 ± 0.1

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equal. On the other hand, the relative importance of the three fragment groups $C_kH_{2k+1}^+$, $C_kH_{2k}^+$ and $C_kH_{2k-1}^+$ varies with pressure. The reason for this is not clear, but the result illustrates that CI spectra from different sources cannot necessarily be directly compared.

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10. The Chemical Ionization of Organic Compounds

2nd Communication[1])

Linear Alkyl Halides

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(21. VII. 75)

Summary. The chemical ionization spectra of linear alkyl halides with up to nine carbon atoms have been studied using water as protonating agent. An alkyl ion with the same number of carbon atoms as the halide is produced. With more than six carbon atoms in the chain, fragmentation becomes important. The results show that excited hydronium ions participate as intermediates and the fragments of the resulting alkyl ions have branched structures.

1. Introduction. – In previous publications, we studied the mass spectral fragmentation by electron impact (EI) of *n*-alkyl ions [2] [3] and showed that this pro-

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[1]) 1st Communication see [1].