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Chemical Ionization Mass Spectrometry. I. General Introduction

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Abstract: The purpose of this paper is to present a new technique in mass spectrometry, chemical ionization mass spectrometry, which is based on the formation of the ions of an unknown material by chemical reactions in the gas phase. A reaction gas is introduced into the ionization chamber of a mass spectrometer at pressures of 1 torr. This reaction gas is ionized and a set of ions is produced which does not react further with the reaction gas. If a small amount of another material is present in the mixture at these high pressures, the stable ions of the reaction gas will react with this second material to produce a spectrum of ions characteristic of the second material. The spectra which are produced by chemical reactions are frequently different from those spectra produced by conventional electron impact methods and are often more useful for determining the structure of compounds and identifying compounds and mixtures than electron impact spectra. The fragmentation patterns of chemical ionization mass spectrometry correspond closely to the structures of the molecules and appear to result from localized attack at reactive centers in the molecule. Reasonable hypotheses are offered for the reactions forming the major product ions of several types of molecules.

The purpose of this paper is to present a new technique of generating mass spectra, chemical ionization mass spectrometry, in which the characteristic ionization of the materials in question is produced by ionic reactions rather than electron impact. These chemical ionization mass spectra will probably be of particular interest for analytical mass spectrometry. In a recent series of papers, observations have been reported of reactions of ions in methane and in mixtures of methane with small concentrations of other compounds at pressures up to 2 torr within the source of a mass spectrometer.[1-3] It is found that the presence of small amounts of certain substances produces very marked changes in the relative concentrations of the ions formed from the methane. These changes are the result of rapid reactions of the product ions of methane with the added material, and there is produced a spectrum of ions which is characteristic of the added substance. Chemical ionization mass spectra are generally quite different and oftentimes more useful than electron impact spectra.

The technique requires a reaction gas which can produce a set of ions which are either nonreactive or only very slightly reactive with the reaction gas itself, but which can react with other materials. At pressures of the order of 1 torr an ion may make roughly 25 collisions within a mass spectrometer source with conventional dimensions, and thus appreciable reaction with small concentrations of the additive may occur. The theory of the method is relatively simple and will be outlined below. The method is certainly applicable for reaction gases other than methane, but the present discussion will be restricted to methane. Generalizations to other reaction gases will be made later.

For the case of methane as the reaction gas, one introduces into the source of the mass spectrometer a mixture of methane and the added material whose spectrum is to be obtained. The pressure of the additive should be very small compared to the pressure of methane, 10^{-3} times that of the methane or less. Under

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(1) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 3289 (1965).

(2) M. S. B. Munson and F. H. Field, *ibid.*, **87**, 3294 (1965).

(3) M. S. B. Munson and F. H. Field, *ibid.*, **87**, 4242 (1965).

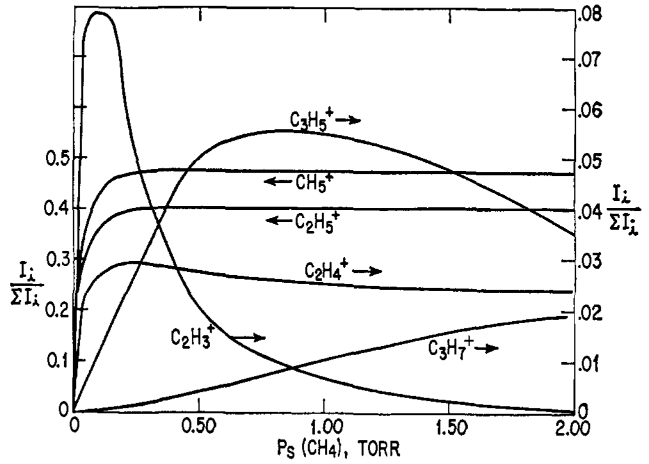

Figure 1. Relative concentrations *vs.* ionization chamber pressure of CH_4.

these conditions, practically all of the electrons passing through the gas within the source will ionize methane, and ionization of the additive by electron impact will be negligible.

$$CH_4 + e \longrightarrow CH_4^+, CH_3^+, CH_2^+, CH^+, \ldots + 2e \tag{1}$$

All of the primary ions of methane react rapidly with methane (at virtually every collision) to give product ions by reactions which are well established.[1]

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \tag{2}$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \tag{3}$$

$$CH_2^+ + CH_4 - \begin{cases} \longrightarrow C_2H_4^+ + H_2 \\ \longrightarrow C_2H_3^+ + H_2 + H \end{cases} \tag{4}$$

$$C_2H_3^+ + CH_4 \longrightarrow C_3H_5^+ + H_2 \tag{5}$$

Small relative concentrations of $C_3H_7^+$, $C_2H_2^+$, $C_3H_3^+$, $C_3H_4^+$, and $C_4H_9^+$ are formed, but these ions do not make an appreciable contribution to the total ionization. As can be seen in Figure 1, above about 0.5 torr for reaction times of the order of microseconds, the relative concentrations of the product ions of methane are substantially independent of pressure. Thus the reactions of the product ions (except $C_2H_3^+$) with methane are relatively slow. Furthermore, if the additive (A) concentration is very small, *i.e.*, $P_A/P_{CH_4} = 10^{-3}$, the reactions of the primary ions of methane with the additive will be negligible when compared with the reactions of the primary ions of methane with methane itself; and the rapid reactions (2–5) for the methane ions will still be predominant.

The major fragment ions of methane produced by electrons of 50 v are CH_4^+ and CH_3^+, which comprise approximately 90% of the total ionization.[4] Consequently, the major secondary ions are CH_5^+ and $C_2H_5^+$, which also comprise about 90% of the total ionization, with $C_3H_5^+$ being roughly half of the remaining ion current (see Figure 1). Since CH_5^+ and $C_2H_5^+$ react slowly or not at all with methane and comprise 90% of the total ionization, it is the reactions of these ions with the additives which produce the major part of the chemical ionization mass spectrum of the additives.

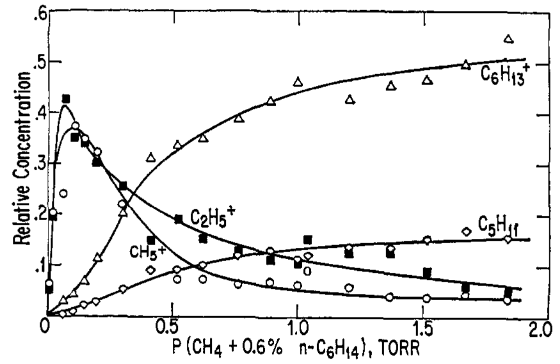

Figure 2. Relative concentrations of ions in methane + *n*-hexane.

From the previous investigations it has been found that CH_5^+ and $C_2H_5^+$ react mostly by proton- or hydride-transfer reactions

$$CH_5^+ + BH \longrightarrow BH_2^+ + CH_4 \tag{6}$$

$$C_2H_5^+ + BH \longrightarrow BH_2^+ + C_2H_4 \tag{7a}$$

$$\searrow B^+ + C_2H_6 \tag{7b}$$

We here let B represent any organic (and possibly inorganic) group. Since CH_4 is a weak Brønsted base,[2] CH_5^+ is a strong Brønsted acid, and proton-transfer reactions to stronger bases than CH_4 will occur. These reactions may be sufficiently exothermic that the BH_2^+ ions, which are produced in reaction 6, will dissociate to form other ions

$$BH_2^+ - \begin{cases} \longrightarrow B^+ + H_2 \\ \longrightarrow A_i^+ + B_i \end{cases} \tag{8}$$

where A_i^+ is one of several possible fragment ions. C_2H_4 is a stronger Brønsted base than CH_4; hence $C_2H_5^+$ is a weaker Brønsted acid than CH_5^+. However, proton transfer may still occur from $C_2H_5^+$ to stronger bases (7a), and this behavior has been observed for water and ammonia.[3] Hydride-transfer reactions (7b), in which $C_2H_5^+$ is acting as a Lewis acid, have also been observed.[5] For both types of reaction of $C_2H_5^+$, it is possible that the product ions may be sufficiently energetic to decompose. One would then expect to observe by this technique a series of fragment ions characteristic of the added material; and, indeed, such characteristic mass spectra are observed.

In addition to the reactions 7a and 7b, $C_2H_5^+$ reacts with some compounds, C_i (commonly ones which contain an O or N atom) by addition in a collision-stabilized process to give an ion of $m/e = MW(C_i) + 29$ (MW = molecular weight). Also for some of these compounds there is a reaction which seems to be a displacement of another hydrocarbon group by the attacking ethyl ion. Similarly $C_3H_5^+$ (present in CH_4 at 1 torr in about 5% concentration; see Figure 1) will react by addition to give ions of $m/e = MW(C_i) + 41$ and ions formed by displacement of hydrocarbon groups. These ions are characteristic of the additive compounds and do not unduly complicate the interpretation of the mass spectra.

Figure 2 is given as an illustration of chemical ionization of an added substance, n-C_6H_{14} (concentration of 0.6%), by CH_4. The maxima and exponential-type decrease (compare with Figure 1) in the relative con-

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

(5) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **68**, 3098 (1964).

centrations of CH_5^+ and $C_2H_5^+$ show that these methane ions are being consumed by a reaction. The corresponding rise in the concentrations of $C_6H_{13}^+$ and $C_5H_{11}^+$, which come from *n*-C_6H_{14}, indicates clearly that reaction (chemical ionization) is occurring between methane ions and *n*-C_6H_{14}. It may be observed from the figure that the relative concentrations of the two products ions ($C_6H_{13}^+$ and $C_5H_{11}^+$) do not change strongly with pressure above 1 torr. Note also that at 1 torr and above a large fraction of the ionization originally present as ions of methane is transferred to the small amount of *n*-C_6H_{14}.

Experimental Section

Apparatus. The mass spectrometer has been partially described previously,[1,6] but a brief description will be given here for reference. The instrument is a 12-in. radius of curvature, 60° magnetic deflection spectrometer with a hot wire electron source. The chamber surrounding the source, electron gun, and ion gun is connected to the section containing the magnetic analyzer only by the ion entrance slit (0.25 × 10 mm), and each section is evacuated by a 4-in. diameter oil diffusion pump (manufacturer's speed designation = 300 l. sec). At a source pressure of 1 torr, the pressure in the analyzer chamber is 2×10^{-5} torr when measured by an ionization gauge on the exhaust line leading to the diffusion pumps. The dimensions of the source electron entrance slit are 0.05 × 3 mm and those of the ion exit slit are 0.05 × 5 mm. The path length of the ions within the source is 2 mm. The ions are expelled from the source by a 1–5 v continuous positive potential on the repeller electrodes. The ion accelerating voltage is generally maintained at 3000 v.

The ionizing electrons are emitted from a hot Ir filament. The emitted current is of the order of tens of microamperes, and the collected current may be hundredths to a few tens of microamperes. The electron beam is magnetically collimated. Electron energies of 70–800 v have been successfully used for the primary ionization of methane, and the higher values are more useful because of the greater penetration of the electrons into the ionization chamber at high pressure. At a constant source pressure the electron current has been maintained constant by automatically controlling either the emitted or the collected current with fair success. No evidence has ever been obtained for diffusion of filament pyrolysis products (if any) back into the ionization chamber, and no deleterious effects of operating for prolonged periods of time (6 months) at 1 torr have been observed. No unusual deposits have been observed in either the ionization chamber or the filament chamber, and operation and maintenance of the mass spectrometer at high pressure is not more difficult than operation and maintenance at conventional conditions.

An electrode which intercepts a small fraction of the unresolved ion beam ($I \cong 10^{-12}$ amp) has been added within the magnetic analyzer chamber. The electron current is adjusted to maintain this value constant (±3%) during the experiments.

The resolved ion current detection system consists of a ten-stage electron multiplier, an Applied Physics Model 36 electrometer, and a Minneapolis-Honeywell 1508 Visicorder with four galvanometers. The dynamic range of the system is 1 to 30,000.

The pressure within the source is measured by a quartz spiral Bourdon gauge (Texas Instruments Corp.), which is attached through a small tube directly to the source. With this device the pressure can be measured with an accuracy of 3–5 μ at 1 torr. The source temperature for these experiments was approximately 180°.

The complete gas handling system consists of two subsystems connected in parallel; that is, gas flows through the gold foil leak associated with each subsystem into a common line which leads to the ionization chamber. The methane is contained in one subsystem, the total volume of which is about 10 l. Typically, a pressure of a few hundred torr within the subsystem will yield a source pressure of 1 torr. The flow out of the reservoir is rapid and the pressure must be maintained constant manually during the course of a measurement. A constancy of ±2% can easily be achieved. It has been found that, in general, research grade methane is satisfactory.

The additive is introduced into the second gas handling subsystem through a porcelain frit covered with gallium. The second gas handling subsystem is a 2-l. vessel maintained at 230°. Since the pressure of methane in the source is 1 torr and somewhat higher in the line leading to the source, it is necessary that the total pressure in the additive vessel be higher than that which is exerted by analytical amounts of additive (~1 μl. of liquid). Consequently, a few torr of methane are added to the additive reservoir to help sweep the additive into the source.

The compounds which were used as additives were obtained from several commercial sources and were used without further purification.

Instrumental Parameters. In order to determine the stability of the total ionization produced by the methane ions and of the distribution of the ions from methane, several repetitive scans were made under identical conditions. The short-term stability of total ionization and methane ion distribution is very good, with an average deviation from the mean of 2–4%.

The total ionizations of nine different low molecular weight additives which were determined as duplicates had reproducibilities of ±0.5 to ±16% with an average for this series of ±7%. The total ionization for *n*-decane was constant within ±5% for a period of about a month. The spectra produced by the chemical ionization technique are not very sensitive to instrumental conditions. Thus it was found that for the two dozen or so compounds for which we have determined replicate spectra under different conditions, the distributions of the ions in the spectra, expressed as percentages of the total ionization, were always constant to better than ±10%.

Additive volumes of 1 to 50 μl. of liquid have been used, depending upon the compounds and the experimental conditions. The size of the sample has little effect on the spectral pattern, except that in some cases for the largest sample size ions of *m*/*e* greater than the molecular weight are formed. Their concentration varies strongly with pressure of the additive, and they are doubtless formed by reaction of the ions of the additives with the additive molecules. The existence of these ions creates an upper limit for the pressures of the additives which can be used. The minimum size sample has not been determined, but spectra have been determined with 1 μl of sample, and the sensitivity can be easily increased by increasing the sensitivity of the electron multiplier. The total ionization of additive observed in the experiments to date have ranged from 1000 to 50,000 divisions, with two divisions distinguishable from noise. Thus sufficient intensity is available for most purposes. The total ionization of the additive is substantially linear in volume of additive for the range 1–10 μl.

Spectra and Discussion

Table I shows the chemical ionization mass spectrum of *n*-hexadecane with methane as the reaction gas and for comparison the electron impact mass spectrum of *n*-hexadecane. These spectra are typical of the spectra obtained for relatively large normal paraffins. The column in Table I headed "CH_4 only" contains the ion currents for the ions present in methane. The relative amounts of these ions are sensitive functions of the purity of the methane and are determined frequently. It is obvious that small contributions from an additive at *m*/*e* 17, 29, and 41 cannot be determined, and normally the mass spectra are reported for ions of *m*/*e* greater than 43 or sometimes 57. A correction must be applied for these ions which are also formed in the methane reaction gas. This correction is applied by assuming that the contribution to any ion current from the methane is a constant fraction of the ionization from methane, independent of the presence of the additive. These mass interferences do not constitute a meaningful restriction on the method, for the chemical ionization technique is most useful for higher molecular weight compounds.

In the absence of complicating effects, one would expect the total ionization to be the same in methane and in methane plus additive, since those ions of methane which react do so to form ions of the additive.

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(6) F. H. Field, *J. Am. Chem. Soc.*, **83**, 1523 (1961).

Table I. Mass Spectra of n-$C_{16}H_{34}$ (Methane Reactant, P_{CH_4} = 1.0 torr)

m/e	Ion	Chemical ionization intensities (chart div)		Relative intensities, % of additive ionization	
		CH_4 only	CH_4 + n-$C_{16}H_{34}$	Chem ionization[a]	Electron impact[b]
17	CH_5^+	25,900	22,500		
18		340	265		
19	H_3O^+	1,470	1,040		
28	$C_2H_4^+$	1,900	1,570		
29	$C_2H_5^+$	25,200	21,700		
30		625	550		
31		292	190		
39	$C_3H_3^+$	80	80		
40	$C_3H_4^+$	145	120		
41	$C_3H_5^+$	5,070	4,300		9.9
42		255	210		2.7
43	$C_3H_7^+$	3,300	2,240		19.7
44		115	90		0.4
55	$C_4H_7^+$	38	53		4.5
57	$C_4H_9^+$	1,560[c]	1,530		20.2
58		90	94		0.9
69	$C_5H_9^+$		9	0.2	1.7
70	$C_5H_{10}^+$		8	0.2	2.0
71	$C_5H_{11}^+$		430	9.1 ± 0.6	11.5
72			29	0.6	0.7
83	$C_6H_{11}^+$		10	0.2	0.9
85	$C_6H_{13}^+$		370	8.4 ± 0.7	7.1
86			30	0.6	0.5
97	$C_7H_{13}^+$		9	0.2	0.5
98	$C_7H_{14}^+$		17	0.3	0.8
99	$C_7H_{15}^+$		275	5.1 ± 0.3	1.6
100			22	0.4	0.1
111	$C_8H_{15}^+$		9	0.2	0.2
112	$C_8H_{16}^+$		8	0.2	0.5
113	$C_8H_{17}^+$		245	4.5 ± 0.3	1.0
114			19	0.3	0.1
125	$C_9H_{17}^+$		6	0.1	0.1
126	$C_9H_{18}^+$		6	0.1	0.5
127	$C_9H_{19}^+$		243	4.2 ± 0.2	0.9
128			24	0.5	0.1
141	$C_{10}H_{21}^+$		216	4.9 ± 0.5	0.7
142			18	0.3	0.1
155	$C_{11}H_{23}^+$		180	2.8 ± 0.3	0.5
156			18	0.3	0.1
169			120	1.9 ± 0.4	0.4
170			15	0.3	...
183	$C_{13}H_{27}^+$		78	1.3 ± 0.1	0.3
184			12	0.2	...
197	$C_{14}H_{29}^+$		63	1.4 ± 0.1	0.1
198			10	0.2	...
211	$C_{15}H_{31}^+$		200	3.9 ± 0.2	...
212			29	0.6	...
225	$C_{16}H_{33}^+$		2,090	36.4 ± 1.7	...
226	$C^{13}C^{12}{}_{15}H_{33}^+$		380	6.6 ± 0.4	0.5
227	$C_2{}^{13}C^{12}{}_{14}H_{33}^+$		31	0.5	...
ΣI_i		67,190	61,740		
$\Sigma I_{n\text{-}C_{16}H_{34}}$			5,229		

[a] Average of six replicates ± average deviation for larger peaks.
[b] API Project 44, "Tables of Mass Spectral Data," No. 1005.
[c] CH_4 was slightly contaminated with i-C_4H_{10}.

This expectation is not rigorously true for the experiments listed here; there is a decrease in total ionization of about 10%. This decrease is greater than we would like and is being studied. However, it does not vitiate the method.

The most striking difference between the chemical ionization and electron impact mass spectra of n-hexadecane is the much larger relative intensity of the chemical ionization $C_{16}H_{33}^+$ (m/e 225) ion (I_{rel} = 36%) than any electron impact C_{16} ion. The chemical ionization spectrum exhibits ions at m/e = 226 and 227, but the intensities of these correspond within experimental error to the intensities to be expected for $C^{13}C^{12}{}_{15}H_{33}^+$ and $C^{13}{}_2C^{12}{}_{14}H_{33}^+$. Thus no parent ion with formula $C_{16}H_{34}^+$ is formed by chemical ionization, and indeed none is to be anticipated from the postulated chemical ionization processes (eq 6–8). However, the concept of a parent ion is a useful one, and we adopt the practice of referring to the ion in the chemical ionization mass spectrum with m/e = MW ± 1 as the quasi-parent ion. Then it may be seen from Table I that in n-$C_{16}H_{34}$ the chemical ionization quasi-parent ion has a relative intensity approximately 70 times that of the electron impact parent ion. Generally, the ions in the chemical ionization mass spectrum are predominantly in the high molecular weight end of the spectrum, whereas the converse is true for the electron impact mass spectrum. The chemical ionization spectrum of n-$C_{16}H_{34}$ is relatively simple, consisting almost entirely of the alkyl ions at each carbon number. Only a few lower molecular weight alkenyl ions $(C_nH_{2n-1})^+$ of quite small intensities mar the homogeneity of ion type found in the spectrum. Electron impact spectra contain appreciable amounts of different ion types (not shown in Table I) at the several carbon numbers. The chemical ionization spectra are consistent with our previous discussion of dissociative proton and hydride transfer.

$$CH_5^+ + n\text{-}C_{16}H_{34} \longrightarrow [C_{16}H_{35}^+]^* + CH_4 \qquad (9)$$
$$[C_{16}H_{35}^+]^* \longrightarrow C_{16}H_{33}^+ + H_2$$
$$[C_{16}H_{35}^+]^* \longrightarrow C_{16-n}H_{33-2n}^+ + C_nH_{2n+2}$$

$$C_2H_5^+ + n\text{-}C_{16}H_{34} \longrightarrow C_{16}H_{33}^+ + C_2H_6 \qquad (10)$$

or

$$C_2H_5^+ + n\text{-}C_{16}H_{34} \longrightarrow [C_{18}H_{39}^+]^* \longrightarrow C_{16-m}H_{33-2m}^+ + C_{m+2}H_{2m+6} \qquad (10a)$$

Reaction 10a is included as a displacement reaction which will be discussed later.

Table II gives the chemical ionization and electron impact mass spectra for a singly branched paraffin, n-propyltridecane ($C_6H_{13}CH(n\text{-}C_3H_7)C_6H_{13}$). The presence of the side chain decreases the electron impact parent ion intensity to a negligibly small value, but the chemical ionization quasi-parent ion ($C_{16}H_{33}^+$) dominates the spectrum (I_{rel} = 35%). Fragment alkyl ions corresponding to cleavage at the branched carbon atom at ($C_{13}H_{27}^+$ and $C_{10}H_{21}^+$) are present in both spectra with enhanced intensities, and in addition in the chemical ionization spectrum fragmentation at the branched carbon produces the olefin ions $C_{13}H_{26}^+$ and $C_{10}H_{20}^+$ with small but significant intensities. The mechanism by which these ions are formed is not understood. However, this olefin ion formation process is observed with other branched alkanes (to be discussed in a subsequent paper), and it doubtlessly will serve as a valuable diagnostic device for the location of branch points in isoparaffins.

It is informative to examine the energetics of the chemical ionization processes in paraffins even though lack of experimental data require that this be done only approximately. For n-hexadecane we write the follow-

Table II. Mass Spectra of 7-*n*-Propyltridecane, $C_6H_{13}CH(n\text{-}C_3H_7)C_6H_{13}$ (Methane Reactant, P_{CH_4} = 1.0 torr)

m/e	Ion	Relative intensities, % of additive ionization Chem ionization	 Electron impact[a]
41	$C_3H_5^+$		8.4
42			2.2
43	$C_3H_7^+$		15.9
44			. . .
55	$C_4H_7^+$		4.9
56	$C_4H_8^+$		2.4
57	$C_4H_9^+$		15.2
58			0.6
69	$C_5H_9^+$	0.3	1.8
71	$C_5H_{11}^+$	6.0	9.8
72		0.3	0.6
83	$C_6H_{11}^+$	0.4	0.8
85	$C_6H_{13}^+$	5.4	8.5
86		0.3	0.6
97	$C_7H_{13}^+$	0.2	0.8
98	$C_7H_{14}^+$	0.06	0.5
99	$C_7H_{15}^+$	4.6	1.6
100		0.3	0.1
111	$C_8H_{16}^+$	0.1	0.5
113	$C_8H_{17}^+$	4.1	0.5
114		0.4	0.04
127	$C_9H_{19}^+$	4.2	0.3
128		0.4	0.03
140	$C_{10}H_{20}^+$	1.7	3.0
141	$C_{10}H_{21}^+$	7.1	1.6
142		0.7	0.2
155	$C_{11}H_{23}^+$	3.9	0.1
156		0.5	. . .
169	$C_{12}H_{25}^+$	2.3	0.1
170		0.3	. . .
182	$C_{13}H_{26}^+$	0.8	1.2
183	$C_{13}H_{27}^+$	4.6	1.4
184		0.6	0.2
197	$C_{14}H_{29}^+$	1.7	0.05
198		0.3	. . .
211	$C_{15}H_{31}^+$	4.1	. . .
212		0.8	. . .
225	$C_{16}H_{33}^+$	34.7	. . .
226	$C^{13}C^{12}{}_{15}H_{33}^+$	6.8	0.03
227	$C_2{}^{13}C^{12}{}_{14}H_{33}^+$	0.6	. . .

[a] API Project 44, "Tables of Mass Spectral Data," No. 591.

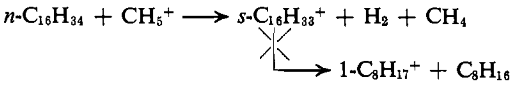
ing thermochemical relations with ΔH values in kcal/mole.

$$n\text{-}C_{16}H_{34} + \begin{cases} CH_5^+ \longrightarrow s\text{-}C_{16}H_{33}^+ + CH_4 + H_2 & \Delta H = -27 \quad \text{(11a)} \\ C_2H_5^+ \longrightarrow s\text{-}C_{16}H_{33}^+ + C_2H_6 & \Delta H = -25 \quad \text{(11b)} \end{cases}$$

$$n\text{-}C_{16}H_{34} + \begin{cases} CH_5^+ \longrightarrow 1\text{-}C_8H_{17}^+ + C_8H_{18} + CH_4 & \Delta H = -12 \quad \text{(12a)} \\ C_2H_5^+ \longrightarrow 1\text{-}C_8H_{17}^+ + C_{10}H_{22} & \Delta H = 0 \quad \text{(12b)} \end{cases}$$

If we assume that rearrangement to form a secondary alkyl ion can occur, the energies for reactions 12a and 12b become −37 and −25 kcal/mole, respectively. The equations are given to represent and be typical of all the dissociative ionizations producing the observed fragment alkyl ions. In these and subsequent calculations, the heats of formation of neutral compounds are obtained from conventional sources, and heats of formation of ions are either taken from Field and Franklin[7] or are approximated using the group equivalent method of Franklin,[8] taking new values for the alkyl ion groups, namely, $-CH_2^+ = 235$, $>CH^+ = 215$, and $\gg C^+ = 205$ kcal/mole.[9] The heat of formation of CH_5^+ is taken as 229 ± 3 kcal/mole as determined recently in these laboratories.[2] Reaction 12b as given is thermoneutral, but a considerable uncertainty in the energetics exists. In view of this and also the fact that reaction 12a is slightly exothermic, we consider that the formation of primary fragment alkyl ions is energetically permitted. The formation of secondary fragment ions would be highly exothermic but requires an ionic rearrangement. Such rearrangements are common in alkyl ions, but the ion which must rearrange in the process we are concerned with is a protonated paraffin ion. The tendency toward rearrangement of this kind of ion is not known and may well be different from those in alkyl ions or paraffin molecule ions. Thus we tentatively postulate that reaction occurs by straightforward bond cleavage.

An alternative mechanism for the formation of fragment alkyl ions can be written, that is, loss of an olefin from the quasi-parent alkyl ion, but the energetics are not favorable. Thus we write as a typical example



$$n\text{-}C_{16}H_{34} + CH_5^+ \longrightarrow s\text{-}C_{16}H_{33}^+ + H_2 + CH_4 \quad (13)$$
$$s\text{-}C_{16}H_{33}^+ \not\longrightarrow 1\text{-}C_8H_{17}^+ + C_8H_{16}$$
$$\Delta H = +18 \text{ kcal/mole}$$

The endothermicity of the reaction depends on the postulate of a primary structure for the fragment alkyl ion. Rearrangement to a secondary ion is a possibility as always, but we believe that the transition state for the formation of the fragment alkyl ion will correspond closely enough to a primary ion structure to make the energy given in reaction 13 applicable.

As was pointed out previously, the $n\text{-}C_{16}H_{33}^+$ ion comprises 36% of the total ionization in *n*-hexadecane, and the remainder is comprised of fragment alkyl ions distributed over a range of carbon numbers. The intensities vary a little with carbon number of the ion, but the variation is small enough to suggest that no strongly specific chemical effects are occurring. We tentatively postulate that the attack by the reacting ion (CH_5^+ or $C_2H_5^+$) occurs at random along the hydrocarbon chain, and the reactions ensuing from the attack are localized at the point of attack. From the relative amounts of quasi-parent and fragment ions, we must conclude that the attacking ion effects C–C bond fission about twice as often as C–H fission in spite of the fact that the molecule contains twice as many C–H as C–C bonds.

It is reasonable to think of the chemical ionization reaction as an electrophilic attack of the reactant ion on the paraffin molecule. The attack occurs preferentially, but not exclusively, at the C–C bond to effect what might be looked upon as an alkyl ion displacement (for example, reaction 12a). Hydride ion abstraction (for example, reaction 11b) occurs to a smaller extent, but it always produces an ion of the same mass (*m/e* 225), and hence a large quasi-parent ion intensity is observed. We may draw an analogy between the postulated electrophilic displacement and abstraction reactions in chemical ionization and the occurrence in condensed phase of nucleophilic displacement and elimination reactions, *e.g.*

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

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

(9) J. L. Franklin, private communication.

$$RCH_2CH_2X + N^- \longrightarrow RCH_2CH_2N + X^- \qquad (14)$$

but also

$$\begin{array}{l} RCH_2CH_2X + N^- \longrightarrow [RC^-HCH_2X] + NH \qquad (15) \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad RCH{=}CH_2 + X^- \end{array}$$

As was mentioned earlier, the decomposition producing the olefin is not observed in chemical ionization. Since, according to our postulate, the relative amounts of H^- abstraction and R^+ displacement are determined by molecular properties which are localized at the point of the electrophilic attack, one might predict as a corollary that the relative amounts of the two modes of reaction will not be much affected by changes in the chain length of the paraffin. This behavior is in fact observed experimentally, for we shall show in a subsequent paper that the relative intensities of the quasi-parent ions are approximately constant in normal paraffins with a wide range of carbon atoms.

In the case of the branched paraffin, 7-N-propyltridecane, we can write

$$C_6H_{13}CH(n\text{-}C_3H_7)C_6H_{13} + CH_5^+ \longrightarrow$$

$$C_6H_{13}CH(n\text{-}C_3H_7)CH_2\overset{+}{C}HC_4H_9 + H_2 + CH_4 \qquad (16)$$
$$\Delta H = -27 \text{ kcal/mole}$$

$$\longrightarrow C_6H_{13}\overset{+}{C}(n\text{-}C_3H_7)\,C_6H_{13} + H_2 + CH_4 \qquad (17)$$
$$\Delta H = -41 \text{ kcal/mole}$$

$$\longrightarrow C_6H_{13}\overset{+}{C}HC_3H_7 + C_6H_{14} + CH_4 \qquad (18)$$
$$\Delta H = -36 \text{ kcal/mole}$$

$$\longrightarrow C_6H_{13}\overset{+}{C}HC_6H_{13} + C_3H_8 + CH_4 \qquad (19)$$
$$\Delta H = -36 \text{ kcal/mole}$$

Approximately the same energies will be obtained using $C_2H_5^+$ as the reactant ion. All of these reactions are obviously energetically allowed. As may be seen from Table II, the mass spectrum of 7-*n*-propyltridecane shows an enhancement in the intensities at *m/e* 183 ($C_6H_{13}C^+HC_6H_{13}$), reaction 18, and *m/e* 141 ($C_6H_{13}C^+HC_3H_7$), reaction 19, compared with the intensities at these *m/e* values in *n*-$C_{16}H_{34}$. In 7-*n*-propyltridecane the intensity at *m/e* 141 is about twice that at *m/e* 183. The intensity enhancement at *m/e* 183 and 141 can be rationalized in terms of our hypothesis: the electrophilic group attacking at the branch-point carbon atom is confronted with a higher proportion of C–C bonds to C–H bonds than exists along a linear chain. In addition, it is of interest that the relative intensities of *m/e* 141 and 183 correspond to the fact that the *m/e* 141 ion can be formed by a displacement reaction in two identical ways since two C_6H_{13} groups exist in the molecule. By contrast the ion with *m/e* 183 can be formed in only one way. In broad outline the spectrum of 7-*n*-propyltridecane is not markedly different from that of *n*-$C_{16}H_{34}$, and we may conclude that the ionic attack on the molecule is still essentially random; that is, the presence of the tertiary carbon atom has little effect on the nature and course of the chemical ionization.

We now consider the chemical ionization mass spectra for four compounds of different types to illustrate other modes of chemical ionization reaction. A number of alcohols and esters have been investigated, and the spectra given are typical for these compound types. As we shall see, for all the compound types the relative intensities of the chemical ionization quasi-parent ions are greater than the electron impact parent, and the chemical ionization fragmentation pattern is relatively simple, tending to be restricted to simple bond cleavages. In these compounds the center of attack appears to be the polar group.

Table III. Mass Spectra of Tri-*n*-butylamine, $(n\text{-}C_4H_9)_3N$ (Methane Reactant, P_{CH_4} = 1.0 torr)

	Relative intensities, % of additive (CI) or total (EI) ionization		
m/e	Chem ionization	Electron impact	Comment
27		4.9	
28		2.3	
29		10.4	
30		4.3	
39		1.6	
41		6.3	
42		4.7	
43		2.3	
44		4.4	
45	0.2	0.2	
55	0.2	1.6	
56		1.1	
57		4.0	
58		1.5	
84		1.3	
86	0.3	1.3	
98		1.3	
100	0.2	7.8	
126	0.1	0.1	
127	0.1	0.0	
128	0.9	0.3	
130	0.8	0.0	
140	0.8	0.3	
141	0.1	0.0	
142	19.9	29.6	$(n\text{-}C_4H_9)_2NCH_2^+$
143	1.8	?	
144	2.0	0.0	
156	2.5	0.3	$(n\text{-}C_4H_9)_2NCH_2CH_2^+$
157	0.5	0.0	
158	0.6	0.0	
168	0.5	0.0	
170	3.5	0.0	$(n\text{-}C_4H_9)_2NCH_2CH_2CH_2^+$
171	0.4	0.0	
172	0.3	0.0	
180	0.3	0.0	
181	0.5	0.0	
182	1.9	0.0	
183	1.5	0.0	
184	23.1	0.0	$(n\text{-}C_4H_9)_2N\overset{+}{C}HC_3H_7$, $(MW - 1)^+$, hydride abstraction
185	10.8	1.6	$(n\text{-}C_4H_9)_3N^+$, $(MW)^+$, charge transfer, corrected for ^{13}C = 7.7
186	21.1	0.0	$(n\text{-}C_4H_9)_3NH^+$, $(MW + 1)^+$, proton transfer
187	2.1	0.0	
210	0.1	0.0	
212	0.3	0.0	
214	1.7	0.0	$(n\text{-}C_4H_9)_3NC_2H_5^+$, addition

The chemical ionization and electron impact spectra of tri-*n*-butylamine are given in Table III. In the region of the molecular weight, by chemical ionization spectrometry, there are three major ions comprising 55% of the total ionization, but by electron impact spectrometry there is only 1.6% as the parent ion. The $(MW + 1)^+$ and $(MW - 1)^+$ ions are caused by proton-transfer and hydride-transfer reactions.

From the existence of the ion at MW + 29 (*m/e* 214) and, to a much larger extent, at MW + 1, it is clear that electrophilic attack occurs on the nitrogen atom of the molecule. In addition, the existence of an ion at MW − 1 indicates that attack on the alkyl radicals resulting in the abstraction of H^- also occurs. Working by analogy with the results for the hexadecanes discussed previously, we might thus expect to observe carbonium ion displacements occurring, and indeed an ion with quite large intensity is observed at *m/e* 142 ($(n\text{-}C_4H_9)_2N^+{=}CH_2$) accompanied by ions of smaller intensities at *m/e* 156 and 170 ($(n\text{-}C_4H_9)_2NCH_2CH_2^+$ and $(n\text{-}C_4H_9)_2NCH_2CH_2CH_2^+$). It is of interest that from the intensities of the ions at *m/e* 183, 170, 156, and 142 we may deduce that in the electrophilic attack of the reactant ion about equal amounts of H^- abstraction and carbonium ion displacements occur. We should point out, however, that the *m/e* 142 ion is the largest one in the electron impact spectrum of the substance, and it is not impossible that in the chemical ionization spectrum this ion is also formed by the decomposition of the molecule ion.

In tri-*n*-butylamine the chemical ionization parent ion is 7.7% of the total ionization. Since the ionization potential of C_2H_5 is 8.3–8.8 v[10] and the ionization potential of tri-*n*-butylamine is 7-8 v,[11] the large relative abundance of parent ion is probably caused by charge exchange of the ethyl ion. This is the only instance of the formation of a molecule ion by chemical ionization that we have encountered. For *n*-octylamine (whose spectra is not shown) $(MW + 1)^+$ = 45.4% of the total ionization, $(MW)^+$ (corrected for ^{13}C) = 0.8%, and $(MW - 1)^+$ = 16.4%. Since the ionization potentials of the primary aliphatic amines are probably greater than 8.5 v and those of tertiary aliphatic amines between 7 and 8 v,[8] the differences indicated for the parent ion between primary and tertiary amines will probably be sufficiently general to allow the isomers to be distinguished by this technique.

Other ions with small intensities are observed in the spectrum, and their origin is not known. However, the purity of the amine is not known (Eastman Kodak White Label of uncertain history), and some of the ions may be from impurities.

Table IV shows a comparison of the chemical ionization and electron impact mass spectra of 1-decanol. Again, chemical ionization produces much ionization in the high molecular weight region and an appreciable amount of the $(MW - 1)^+$ ion, but very little ionization occurs at the actual molecular weight by electron impact. The chemical ionization mass spectra gives predominantly two series of ions, $C_nH_{2n-1}^+$ and $C_nH_{2n+1}^+$, and the most abundant mass in the high molecular weight region is $C_{10}H_{21}^+$, the ion corresponding to the loss of water from the protonated alcohol. Unlike the amine (Table III) there are no protonated molecule ions, $(MW + 1)^+$, formed in the chemical ionization spectrum of 1-decanol. For 2-propanol, protonated molecule ions are observed, but $(MW + 1)^+$ ions were not observed for other alcohols whose spectra have been determined. The spectra of the other alcohols which we have studied are qualitatively similar to that of 1-decanol.

Table IV. Mass Spectra of 1-Decanol, 1-$C_{10}H_{21}OH$ (Methane Reactant, P_{CH_4} = 1.0 torr)

	Relative intensities, % of additive (CI) or total (EI) ionization		
m/e	Chem ionization	Electron impact[a]	Comment
41		11.8	
42		4.3	
43		11.2	
44		3.4	
45		1.2	
47	0.8		
53		0.8	
54		1.4	
55	0.6	8.4	$C_4H_7^+$
56		6.0	
57	9.8	6.7	$C_4H_9^+$
58	0.4	0.8	Isotope
67	0.2	1.8	
68		2.9	
69	5.2	4.6	$C_5H_9^+$
70	0.4	5.8	
71	11.9	3.1	$C_5H_{11}^+$
72	0.7	0.4	Isotope
73	0.2	0.1	Isotope + $C_4H_8OH^+$
81	0.6	1.3	
82	0.3	2.4	
83	9.8	3.4	$C_6H_{11}^+$
84	0.8	2.2	
85	11.4	0.6	$C_6H_{13}^+$
86	0.7	0.0	Isotope
87	0.1	0.0	Isotope + $C_5H_{10}OH^+$
95	0.2	1.0	
97	4.2	1.2	$C_7H_{13}^+$
98	0.4	0.6	
99	4.8	0.2	$C_7H_{15}^+$
100	0.4		Isotope
101	0.1		Isotope + $C_6H_{12}OH^+$
109	0.1	0.4	
111	1.0	0.5	
112	0.3	2.0	
113	0.4		$C_8H_{17}^+$
125	0.6		
127	0.2		$C_9H_{19}^+$
129	0.1		
137	0.1		
138		0.2	
139	2.9		$C_{10}H_{19}^+$
140	0.8	0.1	
141	12.9		$C_{10}H_{21}^+$
142	1.4		Isotope
143	0.1		Isotope + $C_9H_{18}OH^+$
155	0.9		
156	0.1		
157	8.4	0.009	$C_{10}H_{20}OH^+$, $(MW - 1)^+$, hydride transfer
158	0.9	0.002	Isotope, no $(MW)^+$
159	0.1		Isotope, no $(MW + 1)^+$

[a] API Project 44, "Tables of Mass Spectral Data," No. 880.

Energetic considerations provide some information about the chemical ionization reactions occurring in 1-decanol. First, it is to be observed that very small concentrations of oxygen-containing ions other than $C_{10}H_{20}OH^+$ (*m/e* 157) are found. Because of the presence of the polar OH group it is to be expected that the ionic attack will occur predominantly at the OH group to produce a spectrum deficient in oxygen-containing ions. The ion of largest intensity in the spectrum is $C_{10}H_{21}^+$ (*m/e* 141), and this can easily be understood as resulting from the reaction

[10] C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, **41**, 3464 (1964).

[11] K. Watanabe, T. Nakayama, and J. Mottl, "Final Report on Ionization Potentials of Molecules by a Photo-Ionization Method," Army Project No. 5B-99-01-004, Dec 1959, gives values for several amines from which this value is estimated.

$$1\text{-}C_{10}H_{21}OH + CH_5^+ \longrightarrow [1\text{-}C_{10}H_{21}OH_2^+]^* + CH_4 \qquad (20)$$
$$\hookrightarrow 1\text{-}C_{10}H_{21}^+ + H_2O$$
$$\Delta H = -22 \text{ kcal/mole}$$

This reaction is, of course, the one involved in the acid-catalyzed dehydration of alcohols in the condensed phase and is not observed in electron impact ionic chemistry. In general, chemical ionization reactions correspond more closely to condensed phase reactions than do electron impact reactions. If reaction 20 is written as producing a secondary decyl ion by rearrangement, the reaction becomes about 35 kcal/mole exothermic.

The ion with *m*/*e* = MW − 1 = 157, $C_{10}H_{20}OH^+$, is formed in relatively low concentration (8.4%), and we are inclined to attribute this to the predominance of the ionic attack at the OH group. We tentatively postulate that the *m*/*e* 157 ion is formed by H^- abstraction at the 1-carbon atom and predominantly has the structure $C_9H_{19}C^+HOH \rightarrow C_9H_{19}CH{=}O^+H$. It is of interest in this regard that measurements to be reported later on other alcohols indicate that the formation of an ion of *m*/*e* = MW − 1 does not occur unless the C atom to which the OH is bonded is also bonded to an H atom.

The presence in the spectrum of relatively large amounts of alkyl ions and quite small amounts of fragment oxygen-containing ions can be rationalized by postulating that the alkyl ions are produced by secondary fragmentation of the decyl ion produced in reaction 20. The reaction energetics are compatible with this postulate. Thus, for example

$$1\text{-}C_{10}H_{21}OH + CH_5^+ \longrightarrow [1\text{-}C_{10}H_{21}OH_2^+]^* + CH_4 \qquad (21)$$
$$\hookrightarrow 1\text{-}C_{10}H_{21}^+ + H_2O$$
$$\hookrightarrow 1\text{-}C_6H_{13}^+ + C_4H_8$$
$$\Delta H = -2 \text{ kcal/mole}$$

If rearrangement to form a secondary hexyl ion occurs, the reaction becomes much more exothermic. It is to be noted from Table IV that very small amounts of $C_9H_{19}^+$ and $C_8H_{17}^+$ ions are formed, and it is perhaps of significance that the olefins which would be produced in the formation of these ions from $1\text{-}C_{10}H_{21}^+$ (CH_2 and C_2H_4, respectively) are relatively high in energy, especially CH_2. It is possible that the reactions are inhibited for energetic reasons.

Appreciable amounts of alkenyl ions ($C_mH_{2m-1}^+$) are to be found in the 1-decanol spectrum, and we suggest that they are formed by H_2 loss from the alkyl ions. Assuming that the alkenyl ions have a substituted allyl structure, the energetics are exothermic. Thus, for example

$$1\text{-}C_{10}H_{21}OH + CH_5^+ \longrightarrow$$
$$[1\text{-}C_{10}H_{21}OH_2^+]^* + CH_4$$
$$\hookrightarrow 1\text{-}C_{10}H_{21}^+ + H_2O$$
$$\hookrightarrow 1\text{-}C_6H_{13}^+ + C_4H_8$$
$$\hookrightarrow C_6H_{11}^+ + H_2$$
$$\Delta H \cong -14 \text{ kcal/mole}$$
$$\hookrightarrow 1\text{-}C_6H_{11}^+ + C_4H_{10} + H_2O$$
$$\Delta H \cong -44 \text{ kcal/mole} \qquad (22)$$

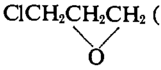
It is necessary to point out that an exothermic reaction producing alkenyl ions from paraffin hydrocarbons can be written, *i.e.*

$$n\text{-}C_{10}H_{22} + CH_5^+ \longrightarrow C_6H_{11}^+ + CH_4 + C_4H_{10} + H_2 \qquad (23)$$
$$\Delta H = -24 \text{ kcal/mole}$$

However, normal paraffins produce only small amounts of alkenyl ions, as may be seen from the spectrum of $n\text{-}C_{16}H_{34}$ in Table I. The occurrence of reaction 22 and the nonoccurrence of reaction 23 is not really disconcerting, for it has long been our observation in gaseous ionic chemistry that the exothermicity of a postulated reaction is a necessary but not sufficient condition for its occurrence.

Table V shows a comparison of the chemical ionization and electron impact mass spectra of epichlorohydrin (i), another compound which forms virtually no parent ion by electron impact. The chemical ionization spectrum is very simple, for only two kinds of ion, ii and $C_3H_5O^+$, comprise 83% of the total epichlorohydrin ionization. The epichlorohydrin molecule is relatively small and contains two electronegative functional groups, and here also the concept of random

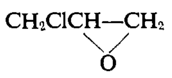
Table V. Mass Spectra of 3-Chloro-1,2-epoxypropane, $ClCH_2CH_2CH_2$ (Methane Reactant, P_{CH_4} = 1.0 torr)

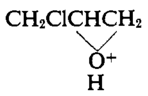


	Relative intensities, % of additive (CI) or total (EI) ionization		
m/*e*	Chem ionization	Electron impact[a]	Comment
26	...	5.2	
27	...	16.9	
28	...	5.5	
29	...	12.6	
30	...	1.1	
31	...	6.8	
35	0.0	0.8	
36	0.0	0.5	
37	0.0	1.0	
38	0.0	0.8	
39	0.0	1.2	
42	0.0	2.0	
43	0.0	0.8	
45	1.0	0.0	
49	0.3	5.9	
51	0.0	1.9	
55	1.0	0.2	
57	38.7	17.6	$C_3H_5O^+$ (MW + 1 − HCl)$^+$
58	1.8	0.6	Isotope
59	4.3	0.1	
62	0.0	3.3	
63	4.2	0.6	$^{35}ClCH_2\text{-}CH_2^+$ (?)
64	0.0	1.0	
65	1.8	0.1	$^{37}ClCH_2\text{-}CH_2^+$ (?)
67	0.2		
69	0.5		
71	0.3		
73	0.4		
75	0.8		$^{35}ClCH_2{-}CH{=}CH^+$, (MW + 1 − H_2O)$^+$
77	0.3		$^{37}ClCH_2{-}CH{=}CH^+$, (MW + 1 − H_2O)$^+$
79	0.3		
81	0.2		
91	0.5	0.03	(MW − 1)$^+$
92	0.0	0.06	(MW)$^+$
93	31.3		(MW + 1)$^+$
94	1.1	0.02	Isotope
95	10.0		(MW + 1)$^+$
96	0.3		Isotope
137	0.7		

[a] API Project 44, "Tables of Mass Spectral Data," No. 772.

attack by the reactant ion is not applicable. Indeed, the spectrum indicates very strongly that attack at the negative groups predominates. While we obviously cannot be sure, it is very tempting to speculate that attack at the oxygen atom results in proton addition to the oxygen. The fact that the oxygen is held by two bonds in a cyclic structure results in stability of the protonated molecule ii (*m/e* 93 and 95), contrasted with


i


ii

loss of H_2O resulting from protonation of the OH group in higher molecular weight alcohols. We may speculate further that attack at the Cl also involves proton transfer but with immediate loss of HCl to form $C_3H_5O^+$ (*m/e* 57) in analogy to the alcohol behavior. It is of interest that in this compound H^- abstraction forming MW − 1 ions is quite small, which may be rationalized as resulting from the extensive polarization of the molecule by the two electronegative functional groups.

The spectrum contains several other small intensity ions whose mode of formation cannot be elucidated. The most intense of these is the ion *m/e* 59, $C_2H_7O^+$, which stoichiometrically cannot be formed from the epichlorohydrin, and therefore must result from an impurity. The reagent (Eastman Kodak, White Label of unknown history) was used without purification, and thus this explanation is reasonable. The ion $ClC_2H_4^+$ (*m/e* 63 and 65) could be formed from the epichlorohydrin (but not by an understood reaction) or from an impurity.

The spectrum was scanned from mass 30 upward, and no evidence was found for the formation of HCl^+ or Cl^+. The failure to observe these species is compatible with the postulate of electrophilic attack at negative centers.

Table VI shows a comparison of the chemical ionization and electron impact mass spectra of *n*-heptyl propionate. There is no ionization in the region corresponding to the molecular weight in the electron impact spectrum, and the distribution of ions is very heavily weighted toward the low-mass region. The chemical ionization spectrum, on the other hand, gives appreciable ionization at the protonated molecule ion and major fragments corresponding to the protonated acid, *m/e* 75, a rearrangement decomposition which is also observed in electron impact and to the propionoxy ion, $C_2H_5CO^+$, from simple bond fission. Ions are found at *m/e* 97, 98, and 99 as may be expected from a heptyl ester. The ions at *m/e* 103 and 115 are alkyl exchange ions formed by a previously unreported process.

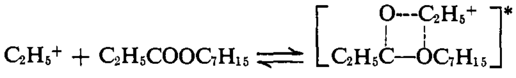
In the light of previous findings, one can expect that the strongly electronegative carboxyl groups will be the focal point of the chemical ionization attack and reactions, and in confirmation one observes the formation of an appreciable amount (12.6%) of MW + 1 ion, $C_2H_5COO(H)C_7H_{15}^+$ (*m/e* 173), formed by proton addition, small amounts of ethyl ion and allyl ion addition, $C_2H_5COO(C_2H_5)C_7H_{15}^+$ (*m/e* 201), and $C_2H_5COO(C_3H_5)C_7H_{15}^+$ (*m/e* 213), and only a quite small amount of H^- abstraction to form the MW − 1 ion.

Table VI. Mass Spectra of *n*-Heptyl Propionate, $C_2H_5COOC_7H_{15}$ (Methane Reactant, P_{CH_4} = 1.0 torr)

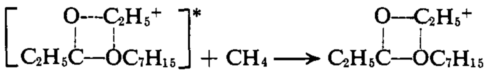
	Relative intensities, % of additive (CI) or total (EI) ionization		
m/e	Chem ionization	Electron impact[a]	Comment
41		6.6	
42	0.0	3.4	
43	0.0	4.8	
55	0.3	4.8	
56	0.0	7.7	
57	15.3	20.5	$C_3H_5O^+$, predominantly
58	0.5	0.8	Isotope
69	0.8	3.3	
70	0.2	5.7	
71	0.2	0.5	
74	0.0	0.4	
75	38.0	7.2	$C_2H_5COOH_2^+$
76	1.3	0.0	Isotope
77	0.2	0.0	
83	2.2	0.7	
84	0.2	0.1	
87	0.1	0.7	
89	0.2	0.0	
91	0.2	0.0	
93	0.1	0.0	
97	6.3	0.5	$C_7H_{13}^+$
98	1.5	3.7	Isotope + $C_7H_{14}^+$
99	4.9	0.3	$C_7H_{15}^+$
100	0.4	0.1	Isotope
101	0.2	0.2	
102	0.2	0.1	
103	7.7	0.0	$C_2H_5CO\overset{H}{O}C_2H_5^+$, alkyl exchange
104	0.5	0.0	Isotope
113	0.1	0.2	
115	0.9	0.2	$C_2H_5CO\overset{H}{O}C_3H_5^+$, alkyl exchange
117	0.1	0.0	
129	0.1	0.0	
131	0.1	0.0	
143	0.1	0.0	
157	0.1	0.0	
171	0.9	0.00	$(MW - 1)^+$, hydride transfer
172	0.0	0.00	$(MW)^+$
173	12.6		$(MW + 1)^+$, proton transfer
174	1.3		Isotope
201	0.8		$C_2H_5C(OC_2H_5)(OC_7H_{15})^+$, ethyl addition
213	1.0		$C_2H_5C(OC_3H_5)(OC_7H_{15})^+$, allyl addition

[a] A. G. Sharkey, Jr., J. L. Shultz, and R. A. Friedel, *Anal. Chem.*, **31**, 87 (1959).

The addition of ethyl and allyl ions to the ester is a novel reaction which produces four different ions in the spectrum. Thus, we can write

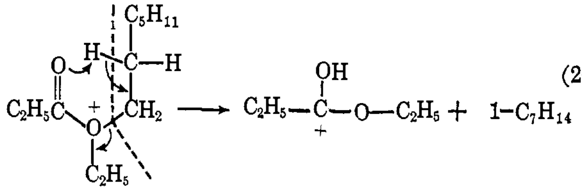

(24)

The dotted lines in the structural formula indicate that the ionic attack may be on either oxygen atom. This transient intermediate can react forward in two ways: (1) stabilization by collision with methane, *i.e.*


m/e 201

(25)

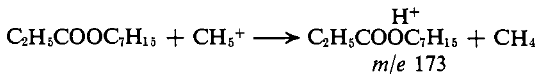
or (2) elimination of C_7H_{14} to form a protonated ethyl propionate ion (alkyl exchange reaction). For this reaction it is convenient to postulate that the ethyl ion–ester complex reacts from a cyclic structure, *i.e.*



(26)

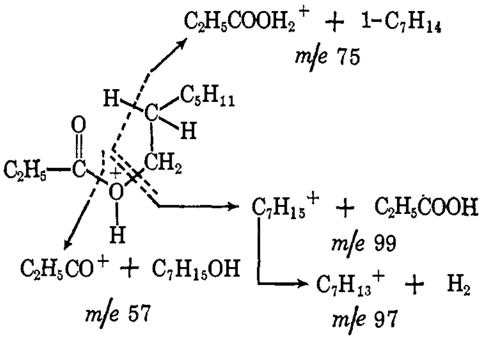
Allyl ion reacts in an analogous manner.

The ion formed by the addition of a proton to the ester also reacts in an analogous manner. Thus we postulate



$$C_2H_5COOC_7H_{15} + CH_5^+ \longrightarrow \underset{m/e\ 173}{\overset{H^+}{C_2H_5COOC_7H_{15}}} + CH_4 \quad (27)$$

Then



(28)

Analysis of Mixtures

It is readily possible to analyze by chemical ionization a mixture of known compounds quantitatively from a knowledge of the relative sensitivities of the compounds in question. One may simply prepare a mixture of known composition to obtain the relative sensitivities and use these values for the analysis of other mixtures of these compounds. Table VII shows representative data for the analysis of mixtures of *n*-dodecane, *n*-tetradecane, and *n*-hexadecane.

Table VII. Analysis of *n*-Alkanes

	Volume %			
	Exptl	Synthesis	Exptl	Synthesis
n-$C_{12}H_{26}$	24.3, 24.3	25.0	49.5, 51.3	48.0
n-$C_{14}H_{30}$	50.4, 50.2	50.0	4.1, 4.4	3.9
n-$C_{16}H_{34}$	25.2, 25.5	25.0	46.2, 44.1	48.0

The agreement between the experimental and known values is certainly satisfactory at the present state of development of this technique. We are currently investigating the degree of constancy with time of the absolute sensitivities of added compounds, and the indications are that the quantitative utility of the method will not be significantly different from that of electron impact mass spectrometry.

Other Reactant Gases

It is possible to use many different gases as reactants and thus to produce spectra from reactant ions of different energy. As an illustration of this, we shall briefly mention two of the other compounds which have been tried as reactant gases, hydrogen and isobutane. The stable product ion in hydrogen is H_3^+, whose heat of formation is not accurately known, but which is a stronger Brønsted acid than CH_5^+, since proton transfer from H_3^+ to CH_4 has been reported.[12] The stable ion in isobutane is $C_4H_9^+$, which is both a weaker proton-transfer and hydride-transfer reactant than $C_2H_5^+$.

The spectra of several compounds have been determined with these reactant gases at 1 torr pressure. In general there is more fragmentation and less of the $(MW \pm 1)^+$ ions with hydrogen than with methane. One would expect that the more exothermic proton-transfer reaction of H_3^+ would produce more fragmentation than the proton-transfer reactions of CH_5^+. $C_4H_9^+$ as a reactant ion produces much less fragmentation than does the combination of CH_5^+ and $C_2H_5^+$ from methane and, as one would expect, produces virtually no ionization with normal paraffins which have no tertiary hydrogens available for abstraction. The effects of different reactant gases will be discussed in more detail in subsequent papers, but even at the present state of development it is clear that chemical ionization provides a flexibility of ionization and spectrum generation which will be of great utility.

Conclusions

We have shown in this paper that is it possible to produce mass spectra which are characteristic of the material in question from reactions of ions at pressures of 1 torr within the source of a mass spectrometer.[13] The spectra which are produced are relatively stable and independent of the operating conditions, and they may be used for both qualitative and quantitative analysis. The spectra which are produced by this chemical ionization technique are very different from those which are produced by conventional electron impact mass spectrometry and are sometimes much more useful for both qualitative and quantitative analysis, particularly of high molecular weight and polyfunctional compounds.

Acknowledgments. The authors are grateful to Donald Becker for his assistance in obtaining some of the spectra.

(12) M. S. B. Munson, F. H. Field, and J. L. Franklin, *J. Am. Chem. Soc.*, **85**, 3584 (1963).

(13) We have in this paper been concerned only with positive ions. However, the technique will doubltless also be applicable for the production of negative ions. A technique for the production of negative ions which bears some resemblance to chemical ionization has been developed by von Ardenne and co-workers. See, for example M. von Ardenne, K. Steinfelder, and R. Tuemmler, *Z. Chem.*, **5**, 287 (1965), and references to earlier work contained therein.