Chemical Ionization Mass Spectrometry

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Chemical ionization mass spectrometry is a form of mass spectrometry wherein the ionization of a substance under investigation is effected by reactions between the molecules of the substance and a set of ions which serve as ionizing reactants. When a substance such as methane is used as the source of reactant ions, the ionization is not governed by Franck–Condon considerations, and the spectra produced are significantly different from those produced by electron impact and field ionization. Different spectra are produced by the use of different ionizing reactants. There is reason to hope that the method will constitute a useful practical method of analysis. The spectra of normal paraffins consist of an intense ion with $m/e = (M - 1)^+$ and approximately equal intensities of alkyl ions with smaller numbers of carbon atoms. In isoparaffins the presence of branching reduces the intensity of the $(M - 1)^+$ ions, but the fragmentation is such as to provide some information about the structure of the molecules. The ionization of the paraffins is described in terms of a theory called the random attack–localized reaction theory, and a semiquantitative method of calculating $(M - 1)^+$ intensities based on this theory has been developed. By contrast, the chemical ionization of propionate esters occurs by specific attack of the reactant ions on the carboxyl group, and the ions found in the spectra are formed by rupture of bonds at the carboxyl group. The number of ions comprising the spectra is relatively small, and the redundancy of information concerning molecular structures is relatively small.

Chemical ionization mass spectrometry[1] is a form of mass spectrometry wherein the ionization of the substance under investigation is effected by reactions between the molecules of the substance and a set of ions which serve as ionizing reactants. Chemical ionization mass spectrometry is thus a branch of gaseous ion–molecule chemistry, but the emphasis is placed primarily upon the generation and determination under identical conditions of the spectra of various substances, paying particular attention to the possibility that a method of practical utility in quantitative or qualitative analysis might result. While there is in chemical ionization work a lively interest in the reactions and mechanisms occurring, no attention has yet been devoted to measurements of types which are usually made in studies of ion–molecule reactions, such as rate constant or cross-section determinations and studies of effect of ion kinetic energy on reaction cross sections.

Chemical ionization mass spectrometry has been carried out in our laboratories using a high-pressure mass spectrometer technique.[1] The reactant ions are formed from one substance by a combination of electron impact ionization and ion–molecule reactions, and the reaction of the reactant ions with the material to be chemically ionized occurs by ion–molecule reactions in the same volume. In almost all of the work that we have done to date, methane has been used as the source of the reactant ions. For these ions (CH_5^+, $C_2H_5^+$, and $C_3H_5^+$; *vide ultra*) the ion–molecule reactions comprising the chemical ionization process involve the transfer of massive entities such as protons, hydride ions, or alkylcarbonium ions. As a consequence, unlike electron impact and photon impact ionization, chemical ionization processes are not governed by Franck–Condon

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

considerations; rather, they must approximate processes which are adiabatic in the physical sense of involving slow, equilibrium adjustments of electronic states and atomic positions. Furthermore, the natures of the reactant ions and of the chemical ionization processes are such that the product ions formed contain even numbers of electrons. This also is in contrast to the formation of odd-electron ions in the initial processes in electron impact, photon impact, and field ionization. The amounts of energy which are involved in the chemical ionization processes tend to be rather low by mass spectrometric standards, although variation occurs depending upon the identity of the reactant material used.

As a result of these factors, one finds that the chemical ionization mass spectra of substances are markedly different from the spectra produced by electron impact ionization on the one hand and by field ionization on the other hand. In general, chemical ionization mass spectra contain relatively small numbers of ion types; that is, the spectra are quite simple. For many compounds the spectra contain significant amounts of ions with m/e values approximately equal to the molecular weights of the compounds. Perhaps of greatest importance is the fact that the chemical ionization mass spectrum of a substance will often reflect or give evidence for different aspects of the structure of a molecule than do either of the other two modes of ionization. Thus the chemical ionization technique adds another dimension to the use of mass spectrometry in molecular structure determination and compound analysis.

An interesting and potentially useful aspect of chemical ionization mass spectrometry is the fact that it gives the experimenter a good deal of flexibility in changing the spectrum of the material investigated by changing the identity of the reactant ions. For the

ions formed from methane, the considerations of the preceding paragraph apply, but under certain circumstances one might wish, for example, to observe the formation and reactions of an odd-electron ion. One can achieve this with chemical ionization by charge exchange, and depending on the identity of the reactant gas, extensive or minimal fragmentation can be produced.

Chemical ionization studies contribute to knowledge of gaseous ionic chemistry, and the contribution has two unique aspects. First, studies made utilizing reactant ions such as those from methane involve, as we mentioned above, the transfer of even-electron charged species, and as such one has gaseous acid–base reactions which are completely analogous to acid–base reactions in condensed phases. Second, the studies are made by investigating the reactions that occur between a given set of reactant ions and many different compounds. The effects of structural properties of the different compounds on the modes of ionization can be investigated just as in solution one can investigate the reactions of a given acid with a series of different bases. This is rather different from the sort of information available from conventional ion–molecule studies wherein the ions which react with the molecules of a given substance are only those which are produced by electron impact from the substance.

In chemical ionization processes the ions are produced and react in the absence of ion–solvent interactions, and the energies available for reaction are high in comparison to energies of condensed-phase reactions. The difference between the gas- and condensed-phase conditions gives rise to gas-phase reactions which are in some aspects different from condensed-phase reactions. These differences contribute to understanding the effects of energy and solvation in ionic organic chemistry. On the other hand, enough similarities exist between reactions in the two phases to show that to a very large extent a common set of principles is obeyed.

The discovery of chemical ionization mass spectrometry was a consequence of a program of investigation of ion–molecule reactions which has been going on in our laboratory for a number of years. In the course of attempting to determine the spectrum of methane at pressures on the order of 1–2 torr, we noticed that traces of impurities had marked effects on the spectra obtained. This initially constituted an undesirable phenomenon, but the investigations undertaken to elucidate it led to the concept of chemical ionization.

The gaseous ionic chemistry of methane has been investigated by many groups,[2-10] and the spectrum is
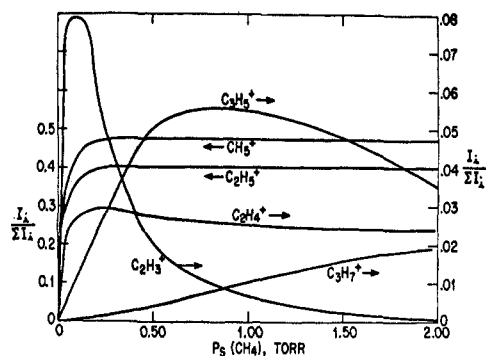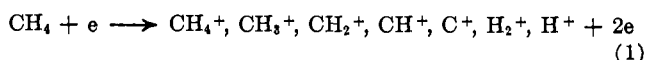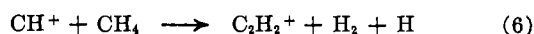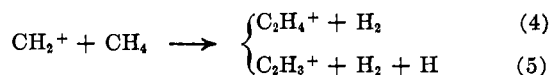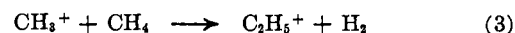

Figure 1. Relative concentrations vs. ionization chamber pressure of CH_4.

given as a function of pressure in Figure 1.[10] The chemical reactions which are involved in producing this spectrum are
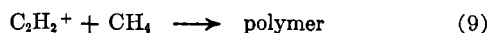
Primary ions

$$CH_4 + e \longrightarrow CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, H_2^+, H^+ + 2e \qquad (1)$$

Secondary reactions

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (2)$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad (3)$$

$$CH_2^+ + CH_4 \longrightarrow \begin{cases} C_2H_4^+ + H_2 & (4) \\ C_2H_3^+ + H_2 + H & (5) \end{cases}$$

$$CH^+ + CH_4 \longrightarrow C_2H_2^+ + H_2 + H \qquad (6)$$

Tertiary reactions

$$C_2H_5^+ + CH_4 \longrightarrow C_3H_7^+ + H_2 \qquad (7)$$

$$C_2H_3^+ + CH_4 \longrightarrow C_3H_5^+ + H_2 \qquad (8)$$

$$C_2H_2^+ + CH_4 \longrightarrow polymer \qquad (9)$$

The chemical ionization studies using methane as a source of reactant ions have been made with 1.0 torr of methane in the ionization chamber. The relative intensities of the ions emerging from the ionization chamber at this pressure can be estimated from Figure 1, and these relative intensities represent the ionic concentrations at the ion-exit slit in the ionization chamber. The sequence of reactions occurring in the ionization chamber is such that the primary ions (reaction 1) are formed by electron impact in the electron beam, and under the influence of the repelling electric field in the ionization chamber they drift toward the ion-exit slit. At the relatively high pressure maintained in the ionization chamber, collisions occur between these ions and methane molecules, and these collisions effect reactions 2–9.

For the sake of simplicity we consider only the two most intense ions produced by these reactions, namely CH_5^+ (47% of the total ionization) and $C_2H_5^+$ (41% of the total ionization). From Figure 1 it is seen that the relative intensities of these ions increase as the pressure

(2) V. L. Tal'roze and A. L. Lyubimova, Dokl. Akad. Nauk SSSR, 86, 909 (1952).

(3) (a) D. P. Stevenson and D. O. Schissler, J. Chem. Phys., 23, 1353 (1955); (b) D. O. Schissler and D. P. Stevenson, ibid., 24, 926 (1956).

(4) F. H. Field, J. L. Franklin, and F. W. Lampe, J. Am. Chem. Soc., 79, 2419 (1957).

(5) V. L. Tal'roze and E. L. Frankevich, Russ. J. Phys. Chem., 34, 1275 (1960).

(6) R. Fuchs, Z. Naturforsch, 16a, 1026 (1961).

(7) S. Wexler and N. Jesse, J. Am. Chem. Soc., 84, 3425 (1962).

(8) F. H. Field, J. L. Franklin, and M. S. B. Munson, ibid., 85, 3575 (1963).

(9) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, ibid., 87, 3289 (1965).

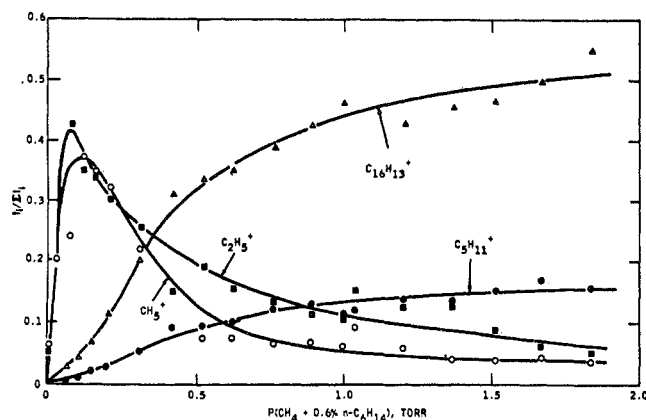(10) F. H. Field and M. S. B. Munson, ibid., 87, 3289 (1965).

Figure 2. Relative concentrations *vs.* ionization chamber pressure of $CH_4 + 0.6\%$ n-C_6H_{14}.

in the ionization chamber is increased to about 0.2 torr, but at higher pressures the relative intensities do not change perceptibly with pressure. Thus we conclude that CH_5^+ and $C_2H_5^+$ are essentially inert in methane. Actually, some reaction of $C_2H_5^+$ occurs to form $C_3H_7^+$ (reaction 7), but the extent of the reaction is too small appreciably to affect the concentration of $C_2H_5^+$ in the ionization chamber.

The reactions forming CH_5^+ and $C_2H_5^+$ are known to occur very rapidly, and from Figure 1 we estimate that at 1.0 torr the CH_4^+ and CH_3^+ primary ions are largely converted to CH_5^+ and $C_2H_5^+$ after traveling about one-fifth of the distance between the electron beam and the ion-exit slit. The CH_5^+ and $C_2H_5^+$ formed drift the remaining distance, and it can be estimated that in the course of their travel they undergo 20–25 collisions with gas molecules before passing out of the ionization chamber. Collisions with methane molecules do not produce new ions, but if one adds to the methane a substance with which the ions can react, collisions which produce a detectable amount of ionization of the added substance will occur. The CH_5^+ and $C_2H_5^+$ ions comprise the reactant ions for the chemical ionization, and the ions produced from the added substance comprise the chemical ionization spectrum of the substance.

The other ions formed in reactions 2–9 also serve as reactant ions. The most important of these is $C_3H_5^+$, which has a relative concentration of 6% of the total ionization.

The effect of the presence of a small amount of additive on the intensities of CH_5^+ and $C_2H_5^+$ is illustrated in Figure 2.[1] n-C_6H_{14} was added to the methane, and the decrease in the intensities of CH_5^+ and $C_2H_5^+$ with increasing pressure above ~0.2 torr is to be contrasted with the constancy shown in pure methane (Figure 1). The decrease in the intensities of the ions from methane is matched by an increase in the intensities of $C_6H_{13}^+$ and $C_5H_{11}^+$ ions, which surely are produced from the n-C_6H_{14}. It has been shown[11] that behavior of this sort is to be expected when reactions are occurring between ions from the substrate and additive molecules, and we

conclude from Figure 2 that a chemical ionization process is producing the hexyl and pentyl ions.

It is seen from Figure 2 that at a pressure of 1 torr most of the total ionization in the system is carried by $C_6H_{13}^+$ and $C_5H_{11}^+$, but this is usually not the case in chemical ionization mass spectrometry. If one has an additive concentration of 0.6%, the partial pressure of the additive at 1 torr total pressure is 0.006 torr, which is high enough for ion–molecule reactions to occur between the additive ions and the additive molecules. In general, we attempt to determine the chemical ionization spectra which result just from the interaction of reactant ions with additive molecules, and thus the concentration of additive is kept appreciably lower than 0.6%. In addition, the relative amounts of additive and reactant should be such that only a negligible amount of ionization of the additive by direct electron impact occurs. When methane is used as a source of reactant ions, satisfactory results have been obtained by operating at a total pressure of 1.0 torr with additive concentrations on the order of 0.1%.

Equipment. Our experiments have been done with the Esso chemical physics mass spectrometer, which has been described previously.[1,12] It is a conventional magnetic deflection instrument with a 12-in. radius of curvature, and it can operate at high pressures because it is fitted with high capacity differential pumping and an ion source which is relatively gas-tight. At a source pressure of methane of 1 torr, the pressure in the region immediately outside the ionization chamber is about 2×10^{-3} torr and that in the analyzer is about 2×10^{-5} torr. The form of the ion peaks that one obtains is quite conventional and acceptable, and a mass resolution of 1600 has been achieved. This is about the same resolving capability as the machine in its present configuration has in low-pressure service, and thus the operation at 1 torr has not resulted in any significant loss in resolution. Our experience is that the use of a mass spectrometer for chemical ionization measurements does not pose special service and maintenance problems.

Results

At the time of writing systematic studies have been made of the chemical ionization mass spectra of normal paraffins and isoparaffins,[13] cycloparaffins,[14] aromatics,[15] esters,[16] C_7H_8 isomers,[17] and olefins.[18] Methane was used as reactant gas in all these studies. A study has been made of charge exchange chemical ionization between benzene and rare gases,[19] and a study of alcohols is currently in progress. In this study the

(11) M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 2332 (1965).

(12) F. H. Field, *ibid.*, **83**, 1523 (1961).

(13) F. H. Field, M. S. B. Munson, and D. A. Becker, Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, pp 167–192.

(14) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **89**, 4272 (1967).

(15) M. S. B. Munson and F. H. Field, *ibid.*, **89**, 1047 (1967).

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

(17) F. H. Field, *J. Am. Chem. Soc.*, **89**, 5328 (1967).

(18) Unpublished data.

(19) F. H. Field, P. Hamlet, and W. F. Libby, *J. Am. Chem. Soc.*, **89**, 6035 (1967).

spectra are generated with ions formed from isobutane. In addition preliminary investigations have been made of other compounds, mostly with methane as reactant but occasionally using other substances.

Limitation of space prevents a discussion of all these compound types, and consequently we shall consider only the studies on the paraffin hydrocarbons and esters. These two compound types involve quite different chemical ionization mechanisms (random and non-random attack by the reactant ions) and represent the range of mechanisms which occur. While the reader will not be able to partake of the complete substance of chemical ionization phenomena, it is hoped that the discussion will at least give something of the flavor of the discipline.

Paraffin Hydrocarbons. The paraffins were the first compounds for which chemical ionization mass spectra were determined, and thus far the largest compound investigated has been n-$C_{44}H_{90}$ (n-tetratetracontane). The chemical ionization mass spectrum of n-$C_{18}H_{38}$ (n-octadecane) is given in Figure 3,[13] and for purposes of comparison, the electron impact spectrum is also given. The dominant ion in the n-$C_{18}H_{38}$ spectrum is $C_{18}H_{37}^+$, which is $(M - 1)$,[+] and the remaining ions are alkyl ions at the different carbon numbers. These fragment alkyl ions are present in approximately equal intensities. The different forms of the spectra produced by chemical ionization and by electron impact lead one immediately to the conclusion that chemical ionization processes in paraffins are quite different from electron impact processes. The spectrum of n-octadecane is typical of the spectra of normal paraffins over a wide range of sizes. Thus the $(M - 1)^+$ ion is as dominant in n-$C_{44}H_{90}$ as it is in smaller paraffins, but by contrast, the M^+ intensities produced by electron impact exhibit a monotonic decrease as the size of the normal paraffin increases.

It is of great interest to speculate on the nature of the ionization mechanisms involved in producing these ions. It is known[20] that $C_2H_5^+$ can effect H^- abstraction reactions with paraffins, and CH_5^+ can transfer a proton to ethane to form $C_2H_7^+$.[21] In ethane part of the $C_2H_7^+$ formed is stable enough to be collected as such, and part of it dissociates to form $C_2H_5^+ + H_2$. There is no convincing evidence for the formation of other stable protonated paraffin hydrocarbons at pressures of about 1 torr, but it is reasonable to think that dissociative proton transfer from CH_5^+ to higher alkanes can occur. Thus we may look upon the methane plasma as comprising a very strong gaseous acid, wherein CH_5^+ is a strong Brønsted acid and $C_2H_5^+$ is a strong Lewis acid. The other ion present in the plasma in significant amounts ($\sim6\%$) is $C_3H_5^+$, and this may be looked upon as reacting as a Lewis acid also.

Actually, these designations are oversimplifications, for one can easily conceive of $C_2H_5^+$ acting as a Brønsted acid by providing a proton with the concomitant forma-
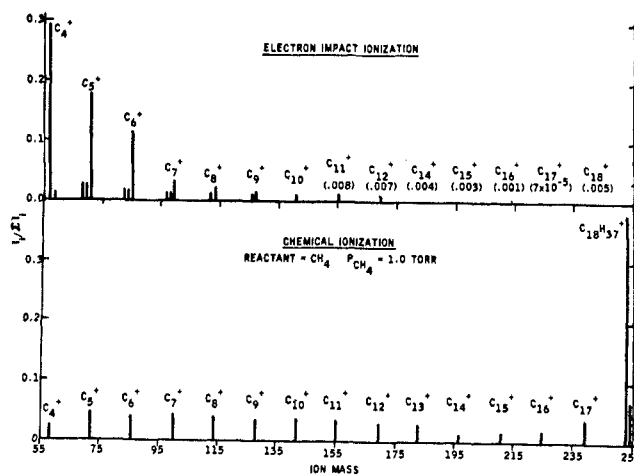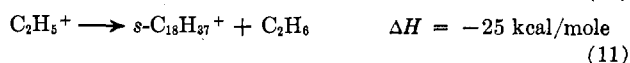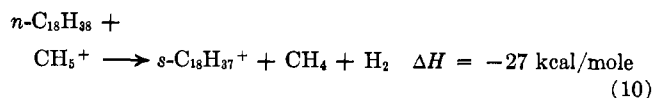

Figure 3. Electron impact and chemical ionization spectra of n-$C_{18}H_{38}$.
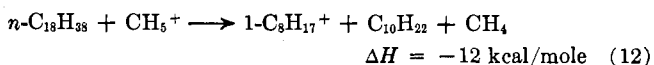
tion of ethylene, and evidence for such a reaction is available. It is perhaps less to be expected, but there is also evidence[14] that CH_5^+ can act as a Lewis acid to abstract H^-, but of course the neutral entity thus formed immediately dissociates into $CH_4 + H_2$. However, for the sake of simplicity we shall consider CH_5^+ to be a Brønsted and $C_2H_5^+$ to be a Lewis acid.

The formation of the $(M - 1)^+$ ion from the normal paraffin occurs by H^- abstraction from the molecule, and this can occur as a direct hydride ion abstraction with $C_2H_5^+$ or a dissociative proton transfer from CH_5^+. Thus, using n-$C_{18}H_{38}$ as an example, we may write

$$n\text{-}C_{18}H_{38} +$$

$$CH_5^+ \longrightarrow s\text{-}C_{18}H_{37}^+ + CH_4 + H_2 \quad \Delta H = -27 \text{ kcal/mole} \tag{10}$$

$$C_2H_5^+ \longrightarrow s\text{-}C_{18}H_{37}^+ + C_2H_6 \qquad \Delta H = -25 \text{ kcal/mole} \tag{11}$$

The reactions as written to produce the secondary octadecyl ion are exothermic,[22] but the formation of the primary octadecyl ion would be slightly endothermic and thus relatively improbable.

Formation of the alkyl ions with $m/e <(M - 1)$ involves carbon–carbon bond fission and is somewhat difficult to explain. Energetic reasons exist for one to question whether these fragment alkyl ions are formed by β fission from a larger alkyl ion such as the $(M - 1)^+$ ion, and it has been suggested [1,13] that the fragment alkyl ions may be formed by a process which may equivalently be looked upon as alkyl ion displacement or the alkide ion abstraction. Thus one would write eq 12 for the formation of the octyl ion from octadecane.

$$n\text{-}C_{18}H_{38} + CH_5^+ \longrightarrow 1\text{-}C_8H_{17}^+ + C_{10}H_{22} + CH_4$$

$$\Delta H = -12 \text{ kcal/mole} \quad (12)$$

(20) F. H. Field and F. W. Lampe, *J. Am. Chem. Soc.*, **80**, 5587 (1958).

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

(22) The significance of the heats of reaction given for these reactions is that it is generally considered in ion–molecule chemistry that endothermic reactions do not occur, or at most have a low probability of occurrence. The reason for this is that even at relatively high pressures in the mass spectrometer ionization chamber the number of collisions occurring between ions and molecules is small by gas kinetic standards, and thus the thermal activation needed to overcome a significant endothermicity cannot occur.

This type of reaction has an appeal in that as an R^- abstraction it constitutes a counterpart to the H^- abstraction process postulated for the formation of $(M - 1)^+$ (eq 10 and 11). Because of the relatively small variation in the intensities of the alkyl ions with $m/e < (M - 1)$ and the lack of dependence of the $(M - 1)^+$ ion intensity on molecule size, it has also been suggested[1,13] that the chemical ionization process in normal paraffins may be conceived of as a random attack of the reactant ions along the length of the alkane chain which results in an electrophilic reaction localized at the point of attack. This attack can involve the electrons in a C–H bond, giving H^- abstraction, or the electrons in a C–C bond, giving alkide ion abstraction.

In terms of these concepts a very simple rationale can be given for the form of the chemical ionization mass spectra of normal paraffins. One postulates that the attack of the reactant ions on the electrons in C–H bonds occurs with equal probability for all of the C–H bonds except the primary bonds and that the probability of attack on all the C–C bonds is the same (but not necessarily the same as the probability of the attack on the C–H bonds). However, the attack on different C–C bonds in the molecule produces fragment alkyl ions of different m/e values, but attack on the different C–H bonds always produces an ion of the same m/e value, that is, $(M - 1)^+$. Thus $(M - 1)^+$ is the largest ion in the spectrum, and from a comparison of the relative intensity of this ion with the sum of the intensities of all the fragment alkyl ions, one concludes that attack of the reactant ions on C–C electrons occurs twice as often as attack on C–H electrons. Since large paraffins contain approximately twice as many non-primary C–H bonds as C–C bonds, one concludes that the inherent probability of C–C attack is approximately four times that of C–H attack.

The chemical ionization mass spectra of a number of branched paraffins containing from 9 to 30 carbon atoms have been determined.[13] The salient feature of their spectra is that the intensities of the $(M - 1)^+$ ions decrease with increased branching in the molecule. However, the decrease in the $(M - 1)^+$ intensity in chemical ionization is not so precipitous as the decrease of M^+ in electron impact, but it has been asserted that chemical ionization fragmentation is more extensive than that observed in field ionization.[23] However, the extent of fragmentation in both chemical ionization and field ionization depends strongly upon experimental conditions, particularly temperature, and a significant amount of the reported difference in the extent of fragmentation may result from differences in experimental conditions.

As an example of the spectrum of a branched compound we give in Figure 4 the chemical ionization and electron impact spectra of 7-n-propyltridecane. The intensity of the $(M - 1)^+$ ion in chemical ionization is only slightly lower than the $(M - 1)^+$ ions in normal

(23) H. D. Beckey, *J. Am. Chem. Soc.*, **88**, 5333 (1966).
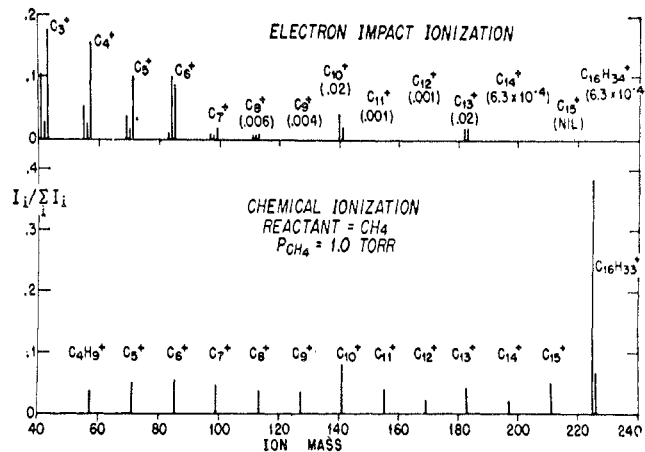

Figure 4. Electron impact and chemical ionization spectra of 7-n-propyltridecane.

compounds, and in general it is found that the presence of a single branch in the paraffins does not change the intensity of the $(M - 1)^+$ very much. It may be seen in Figure 4 that the intensities of the m/e 183 ion $(C_{13}H_{25}^+)$ and m/e 141 ion $(C_{10}H_{21}^+)$ are greater than the intensities of the alkyl ions having one carbon atom more or less than these ions. These ions are formed by fragmentation at the branch point in the molecule, and the enhanced intensity constitutes evidence for the presence of the branch point. Similar behavior is observed in electron impact ionization.

The enhanced intensities of the branch point ions can be accounted for most easily in terms of the occurrence of a β-fission process. Thus we may write eq 13 for the formation of the m/e 141 ion from 7-n-propyltridecane. Reaction 13 is exothermic, in contrast
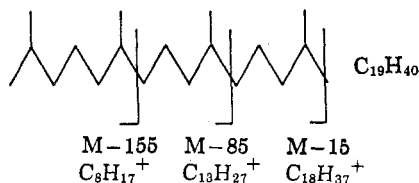

$$\text{(13)}$$
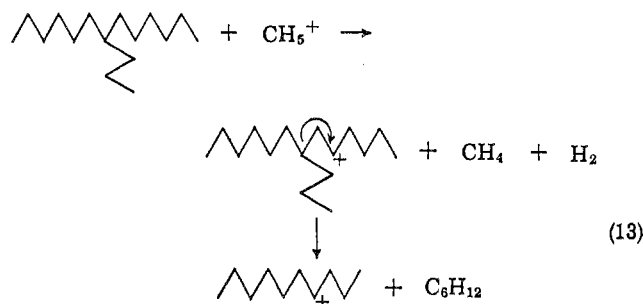
with the endothermic β-fission found in normal paraffins. For compounds containing quaternary carbons, tertiary carbonium ions are formed by the β-fission process, and the reactions analogous to (13) are appreciably more exothermic. Because of the exothermicities the processes have high probabilities, and this contributes in turn to the lesser stability of $(M - 1)^+$ ions in branched paraffins as compared with those in normal paraffins.

The relatively high intensities found in most paraffins for the $(M - 1)^+$ ions and the fact that the spectra reflect the presence of branch points in the molecules mean that the chemical ionization technique has a considerable potential for the analysis of paraffin

hydrocarbons. The $(M - 1)^+$ ion gives information about the molecular weight of the molecule (or the molecular weight distribution in a mixture of molecules), and the enhanced intensities observed at the branch points can be used to deduce information about the structure of the molecule.

It has been pointed out[24] that this technique will be of value in the analysis and characterization of isoprenoid hydrocarbons, which are of biogeochemical significance. Thus pristane exhibits a large $(M-1)^+$ intensity (10% of the total pristane ionization) and enhanced intensities at the mass numbers corresponding to $(M - 15)^+$, $(M - 85)^+$, and $(M - 155)^+$. These ions are formed by fragmentation at the branch points as indicated in the structure of the molecule given above. A similar behavior has been found[13] for the isoprenoid hydrocarbon squalane (2,6,10,15,19,23-hexamethyltetracosane). In both compounds the $(M - 15)^+$ intensity is relatively large, which reflects the fact that both pristane and squalane contain a large number of methyl branches.

The intensity of the $(M - 1)^+$ ion depends strongly upon the structure of the paraffin, with the intensity of the ion decreasing as the degree of branching in the molecule increases. It is possible to rationalize this behavior in terms of the random attack–localized reaction concept of chemical ionization processes.[13] Since the $(M - 1)^+$ ions are formed by removing a hydrogen from the parent paraffin molecule by a localized reaction, it is reasonable to postulate that the intensity of the $(M - 1)^+$ ion formed from a given paraffin hydrocarbon will depend upon the number of hydrogens that are available for removal. Primary hydrogens are not available and are excluded from the counting, and we saw previously that hydrogens removed from carbons to a branch point produce $(M - 1)^+$ ions which have a high probability of decomposing by C–C fission. Thus these hydrogen atoms are also excluded from the counting.

The $(M - 1)^+$ intensities calculated[13] using these considerations are given in Table I along with the observed intensities for comparison. While there are some variations from compound to compound in the agreement between the two sets of intensities, by and large the trends in the calculated values tend to parallel those in the observed values. The agreement is good enough to indicate the approximate validity of the postulates made concerning the ionization and dissociation of paraffins by the chemical ionization technique. Furthermore, even though the calculation is a crude one, it may be of some practical predictive value. Thus on

(24) E. Gelpi and J. Oro, *Anal. Chem.*, **39**, 388 (1967).

Table I
Calculated and Experimental $(M - 1)^+$ Intensities

Compound	I, calcd	I, obsd
(structure)	0.12	0.20
(structure)	0.61	0.94
(structure)	0.020	0.019
(structure)	0.023	0.076
(structure)	0.080	0.057
(structure)	0.099	0.092
(structure)	0.12	0.045
(structure)	0.00	0.005
(structure)	0.00	0.02
(structure)	0.00	0.006
(structure)	0.064	0.002
(structure)	0.11	0.099[a]
(structure)	0.15	0.12

[a] From ref 23.

the basis of the agreement between the calculated and observed intensities for both pristane and squalane, it appears that the $(M - 1)^+$ ion intensities from acyclic isoprenoid hydrocarbons will be given with reasonable accuracy by these considerations.

The intensities of $(M - 1)^+$ ions from cycloparaffins can similarly be calculated using a simple procedure of counting hydrogens. In addition, in cycloparaffins and aromatics the $(M - 15)^+$ ions, which are formed by methide ion abstraction, can be calculated by counting the number of methyl groups in the molecule. All of these calculations are based on the random attack–localized reaction concept, and the concept would appear to have some degree of generality for hydrocarbons.

Esters. We now consider the chemical ionization behavior of a nonhydrocarbon class of compounds, namely, esters of carboxylic acids.[16] The spectrum of *n*-heptyl propionate, which is typical of the spectra observed for alkyl propionates, is given in Table II. It may be seen that the intensity of the $(M - 1)^+$ ion is quite small (0.006), and low intensities have been found for this ion in all of the esters studied. The average $(M - 1)^+$ intensity for 14 propionate esters is 0.004. A further inspection of Table II shows that it

Table II
Relative Ion Intensities for n-Heptyl Propionate[a]

m/e	Formula	Significance	Intensity
213	$C_2H_5C\underset{OC_7H_{15}}{\overset{O\cdots C_3H_5^+}{}}$	$(M + C_3H_5)^+$	0.005
201	$C_2H_5C\underset{OC_7H_{15}}{\overset{O\cdots C_2H_5^+}{}}$	$(M + C_2H_5)^+$	0.001
173	$C_2H_5C\underset{OC_7H_{15}}{\overset{O\cdots H^+}{}}$	$(M + 1)^+$	0.050
171	$C_2H_5C\underset{OC_7H_{14}^+}{\overset{O}{}}$	$(M - 1)^+$	0.006
117	$C_7H_{15}OH_2^+$		0.006
115	$C_2H_5C\underset{OC_3H_5}{\overset{O\cdots H^+}{}}$ and/or $C_7H_{15}O^+$	Alkyl exchange in ester	0.031
103	$C_2H_5C\underset{OC_2H_5}{\overset{O\cdots H^+}{}}$	Alkyl exchange in ester	0.090
99	$C_7H_{15}^+$	Alkyl ion from alcohol	0.040
98	$C_7H_{14}^+$	Olefin ion from alcohol	0.015
97	$C_7H_{13}^+$	Alkenyl ion from alcohol	0.088
75	$C_2H_5C\underset{+}{\overset{OH}{}}{OH}$	Protonated acid	0.39
57	$C_2H_5CO^+$	Propionyl ion	0.16

[a] CH_4 reactant, $P(CH_4) = 1.0$, torr; mol wt of $C_2H_5COOC_7H_{15}$, 172.
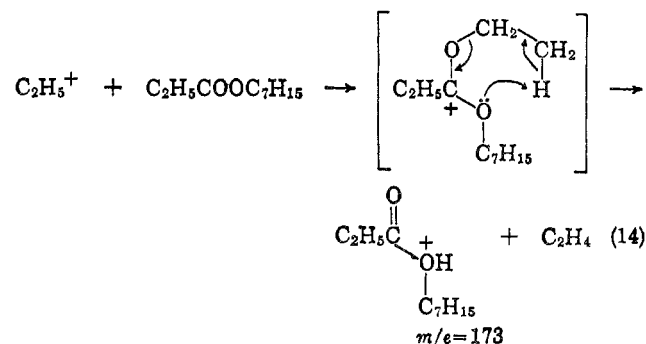
contains no ions formed by the rupture of the C–C bond; rather, all the fragmentation processes involve C–O, C–H, or O–H fissions. It is clear that neither hydride abstraction nor alkyl ion displacement reactions, such as are found in the paraffins, occur to any significant extent in spite of the fact that heptyl propionate contains a long alkyl chain.

Such behavior is hardly to be expected on the basis of the random attack–localized reaction concept, and it is clear that for esters the concept of random attack by reactant ions must be abandoned. Hamill and co-workers[25] have shown that the presence of a permanent dipole in a molecule markedly increases the cross section for ion–molecule reactions. It is probable that in the chemical ionization of esters the attacking ions will be very strongly attracted to the polar carbalkoxy group in the molecule.

For the alkyl propionates all the major features of the observed chemical ionization mass spectra can be explained by reactions which follow attack of the reactant ions (CH_5^+, $C_2H_5^+$, and $C_3H_5^+$) on the carbalkoxy group. One observes in Table II that a moderate

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

amount of $(M + 1)^+$ ion is formed in n-heptyl propionate, and traces of $(M + C_2H_5)^+$ and $(M + C_3H_5)^+$ are also formed. The $(M + 1)^+$ ions are surely formed by proton transfer from CH_5^+ and they possibly also result by proton transfer from $C_2H_5^+$ and perhaps even $C_3H_5^+$. The intensities of $(M + C_2H_5)^+$ and $(M + C_3H_5)^+$ are quite low, which suggests that reactions subsequent to the addition of these ions occur. We shall see that the alkyl exchange reactions producing the m/e 103 and 115 ions constitute such reactions, and proton transfer is also quite probable.

The proton or carbonium ion which is added to the carbalkoxy group can be bonded either to the carbonyl or the ether oxygen, and for most of the reactions there is no reason to favor one type of addition over the other. Therefore, in Table II possible coordination to either of the oxygens is represented. Protonation by $C_2H_5^+$ ion would be expected on energetic grounds to occur by the reaction producing C_2H_4 rather than CH_3CH as neutral product, and this can be thought of as occurring most easily by means of a mechanism involving a cylic intermediate (eq 14). A reaction involving initial
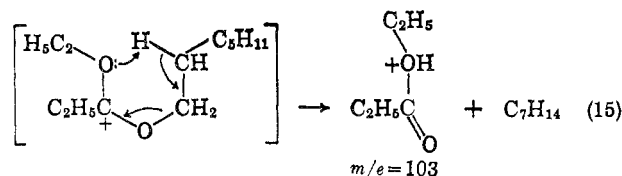
$$C_2H_5^+ + C_2H_5COOC_7H_{15} \longrightarrow \left[C_2H_5C\overset{CH_2}{\underset{\overset{+}{O}}{\overset{O}{}}}\underset{C_7H_{15}}{\overset{CH_2}{}}H \right] \longrightarrow$$

$$C_2H_5\overset{O}{\underset{\underset{C_7H_{15}}{OH}}{C}} + C_2H_4 \quad (14)$$

$$m/e = 173$$

attack of the ethyl ion on the ether oxygen of the ester can also be written.

The intermediate written in eq 14 is of the form

$$C_2H_5C\underset{+}{\overset{OR_1}{}}{OR_2}$$
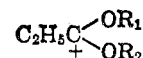
and proton transfer from either alkyl group may be expected. When the proton transfer is from the heptyl group a reaction (eq 15) analogous to eq 14 occurs.

$$\left[\begin{array}{c} H_5C_2 \\ C_2H_5C \end{array} \underset{O}{\overset{O}{}} \underset{CH_2}{\overset{H\ CH\ C_5H_{11}}{}} \right] \longrightarrow C_2H_5\overset{C_2H_5}{\underset{O}{C}}{+OH} + C_7H_{14} \quad (15)$$

$$m/e = 103$$

The ion formed in reaction 15 is the m/e 103 ion which is observed in a spectra of all the alkyl propionates, and and the over-all process constitutes an alkyl group exchange which may be looked upon as the gas-phase analog of condensed-phase ester-exchange processes. Exchange with the $C_3H_5^+$ ions which exist in the methane plasma produces the ion

$$\cdot C_2H_5C\underset{O}{\overset{C_3H_5}{\overset{O}{}}}H$$

$$m/e = 115$$
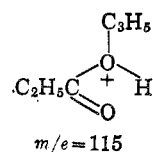
which is also found in the spectrum of all the alkyl propionates.

Protonation at the carbonyl group probably does not promote further decomposition of the ester molecules and contributes solely to the intensity at $(M + 1)^+$, but protonation (and also alkylation) at the ether carbon can induce a number of important reactions. The most important of these is a reaction (eq 16) analogous to reactions 14 and 15 which produces protonated propionic acid. For all save two of the alkyl propionates studied

$$CH_5^+ \; + \; C_2H_5COOC_7H_{15} \; \longrightarrow$$
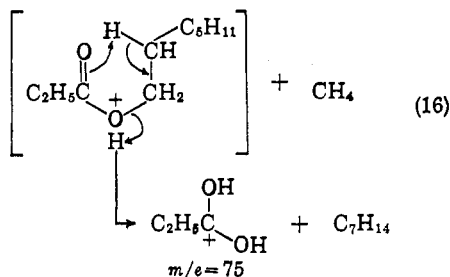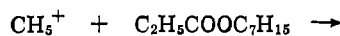
the protonated propionic acid ion $(m/e\ 75)$ is of high intensity, and for a number of the compounds it is the most intense ion in the spectrum. Thus reaction 16 is one that occurs with a high probability. Two other reactions of significance stemming from the intermediate written in reaction 16 involve heterolytic bond fission at the protonated oxygen (eq 17, 18a, b). Note that both
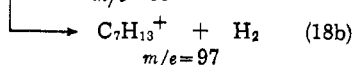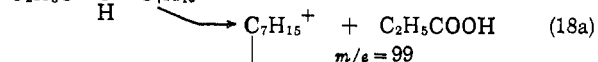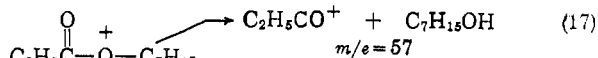
heptyl and heptenyl ions are formed, the latter presumably as a decomposition product of the former.

The chemical ionization spectra of the alkyl esters of propionic acid contain a relatively small number of ions, and it is of interest that almost all of the ions found in the spectra give some information concerning the identity and structure of the ester producing the spectrum. The amount of redundancy in the information contained in the spectra is relatively small. The $(M + 1)^+$ ions provide information concerning the molecular weight. The acyl ions and the protonated acid ions give information about the identity of the acid groups, and the alkyl and alkenyl ions give information about the alcohol groups.

Conclusion

Chemical ionization mass spectrometry is still very new, and the determination of the extent of its utility, both scientific and practical, will require much further work. However, on the basis of the results obtained so far we are quite sanguine about the prospects. Of interest and potential utility is the fact that different

substances can be used as the reactant gas, and these different reactants will generate different mass spectra with a given additive substance. One can expect in this way to obtain more information about a substance than could be obtained from a single spectrum alone.

As was mentioned earlier all but one of the systematic studies done in our laboratory so far have utilized methane as the reactant, and only a few individual measurements have been made with other reactants. However, the measurements which have been made show clearly that the expectations that different reactants will produce markedly different spectra are borne out in fact. The compounds which thus far have been used as reactants are (in addition to methane) propane, isobutane, water, methanol, rare gases, and mixtures of rare gases in benzene. The major ions in propane and isobutane are s-$C_3H_7^+$ and t-$C_4H_9^+$, respectively, and they react primarily by hydride ion abstraction. t-$C_4H_9^+$ is a milder reagent than s-$C_3H_7^+$, which in turn is milder than $C_2H_5^+$ found in methane, and the degree of fragmentation of the additive materials is less with these reactants than with methane.

Water and methanol form almost exclusively protonated entities, which can be monomers, dimers, trimers, etc., depending upon the identity and pressure of the reactant gas. These are relatively weaker Brønsted acids than CH_5^+, and different spectra are generated than with methane. It is particularly interesting that we have been able to carry out a selective ionization using water as a reactant, for in an equimolar mixture of 1-decanol and n-decane, extensive ionization of the decanol was effected (to produce predominantly $(M + 1)^+$ and $(M + H_3O)^+$), whereas no ionization of the decane occurred at all. Clearly this ability to effect differential ionization of compound types will be of great practical importance.

The rare gases act as reactants by abstracting an electron from the material to be ionized, producing an odd-electron ion. The spectra produced then tend to be somewhat similar to those produced in electron impact, although the degree of fragmentation depends strongly upon the identity of the rare gas used. Xenon produces the least fragmentation and helium the most. In a mixture such as benzene and xenon, it appears that a kind of cascade phenomenon occurs.[19] Thus most of the original ionization occurs in the xenon, which then charge transfers to the benzene, which in turn can ionize the additive of interest. Presumably less fragmentation would be effected in this process than if the additive were ionized directly by the xenon, but experimental evidence on this system is very scanty.