

Ion Enthalpies and Their Application in Mass Spectrometry†

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The experimental determination of ionization and appearance energies is discussed, together with the calculation of heats of formation of ions. Results are presented for the ions $[C_nH_{2n+1}]^+$, $[C_nH_{2n+2}N]^+$ and $[C_nH_{2n+1}O]^+$. The low temperature (~ 350 K), low energy (12.1 eV) mass spectra of some alkanes, amines and alcohols are presented and discussed.

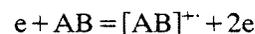
INTRODUCTION

In this paper I wish to discuss primary ion mass spectrometry, which with apologies to Professor Beynon¹ I will call PIMS No.2, carefully to distinguish it from photoionization mass spectrometry (PIMS No. 1). By primary ion mass spectrometry, I mean the observation of spectra of daughter ions produced only from the molecular ion. The structure of such daughter ions can often be inferred from the energetics of the ionization process, as I shall show. However, before considering the mass spectra, I want to say something about the determination of appearance energies of ions, the results obtained and their use in estimating the heats of reaction of fragmentation processes. The choice of electron energies of 50 eV or 70 eV for running mass spectra was decided largely on the basis that fragmentation patterns did not vary very much with electron energy over such an energy range. Thus, this choice was admirably suited for quantitative analysis. On the debit side, so much energy may be imparted to the ions that several generations of daughter ions may be produced. The superfluity of peaks obtained under such conditions has long been regarded as an embarrassment to the mass spectrometrists interested in structural interpretation. In fact, in assigning structure, the minimum number of peaks containing the relevant information is the desired goal. This is the basis of the art of interpretation as practised by the masters, who are able to disregard the irrelevant peaks and concentrate upon the relevant ones. However, this is not so easy for the novice, since the method depends upon widespread experience of the fragmentation of many different classes of molecules. Thus, any attempt to simplify the mass spectrum of a compound is welcome. An excellent example of the power of the approach comes from the beautiful work of Spiteller and his colleagues² on triacontane ($C_{30}H_{62}$). At 70 eV and ~ 500 K the spectrum ends with ions of about half the molecular

weight (Fig. 1). However, if the energy is dropped to 12 eV and the temperature to 350 K, the spectrum is readily interpretable, namely successive losses of 29, 43, 57, 71 (Fig. 2).

Energetics

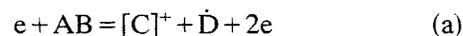
Dealing first with the energetics of ionization and fragmentation, the ionization energy of a molecule $I(M)$, refers to the least energy at which the process



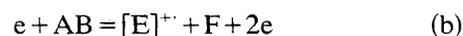
occurs. If the process is from the ground state of the molecule to the ground state of the molecular ion it is the *adiabatic ionization energy* $I_A(M)$. If the final state is vibrationally excited, as determined by the Franck-Condon principle it is the *vertical ionization energy* $I_V(M)$. The heat of formation of the molecular ion $\Delta H_f([M]^+)$ is then given by

$$\Delta H_f([M]^+) = I_A(M) + \Delta H_f(AB) \quad (1)$$

In the case of fragmentation processes



or



the lowest energy at which $[C]^+$ or $[E]^+$ appears is known as the appearance energy, $A([C]^+)$ or $A([E]^+)$. Corresponding to (1) we have

$$\Delta H_f([C]^+) = A_A([C]^+) - \Delta H_f(\dot{D}) + \Delta H_f(AB) - \epsilon \quad (2)$$

or

$$\Delta H_f([E]^+) = A_A([E]^+) - \Delta H_f(F) + \Delta H_f(AB) - \epsilon$$

in the case of the adiabatic appearance energy being measured. The term ϵ includes the kinetic energies of the ion and the neutral, together with any excitation energy of the ion or the neutral and the reverse critical energy (ϵ_r). Given the heats of formation of the relevant species, then a heat of reaction (ΔH) can be

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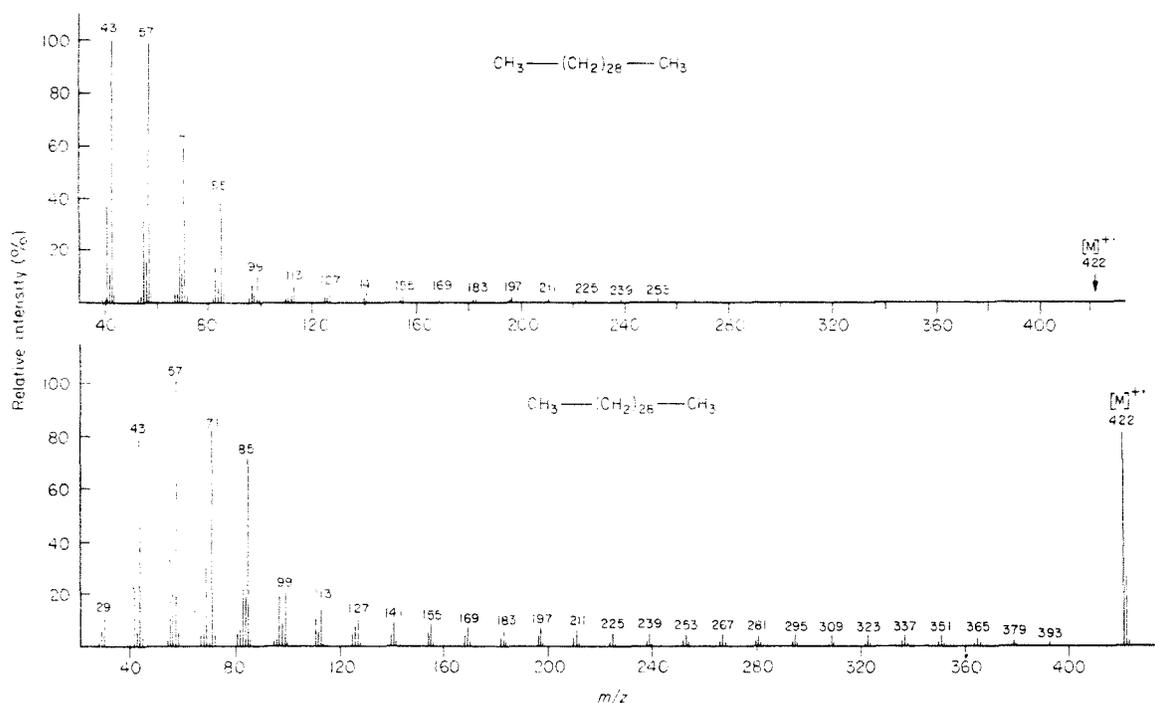


Figure 1. (a) The mass spectrum of triacontane at 70 eV and ~500 K; (b) The mass spectrum of triacontane at 70 eV and ~350 K (after Spittler *et al.*²).

calculated from (3)

$$\begin{aligned} \Delta H([\text{C}]^+) &= \Delta H_f([\text{C}]^+) + \Delta H_f(\text{D}) - \Delta H_f(\text{AB}) \\ \Delta H([\text{E}]^+) &= \Delta H_f([\text{E}]^+) + \Delta H_f(\text{F}) - \Delta H_f(\text{AB}) \end{aligned} \quad (3)$$

and

$$\begin{aligned} \Delta H([\text{C}]^+) &= A_A([\text{C}^+]) \\ \Delta H([\text{E}]^+) &= A_A([\text{E}^+]) \end{aligned} \quad (4)$$

provided $\epsilon = 0$. For many processes it would appear that $\epsilon_r = 0$, which may be explained by tunnelling through the critical hump.³ Thus, Lossing⁴ has shown that the ion $[\text{C}_3\text{H}_5]^+$ produced from eight different sources leads to a unique value for $\Delta H_f([\text{C}_3\text{H}_5]^+)$, despite the fact that in some cases, complex rearrangement processes are involved (Table 1).

Measurement of ionization and appearance energies

The use of the electron monochromator developed by Lossing⁵ to measure ionization and appearance energies is by now well known. Energy selection of the electrons is achieved by the use of a double hemisphere with its attendant lens systems. The general design of our equipment is shown in Fig. 3, the completed hemisphere system in Fig. 4 and the apparatus in Fig. 5. Ion detection is achieved by a quadrupole mass filter used with pulse counting. A PDP8 system puts a ramp (0.001 V–0.005 V steps) on the electron energy, and collects and stores the ion count and finally plots the ion current as a function of electron energy. The vanishing current method is used to detect the onset (Fig. 6).

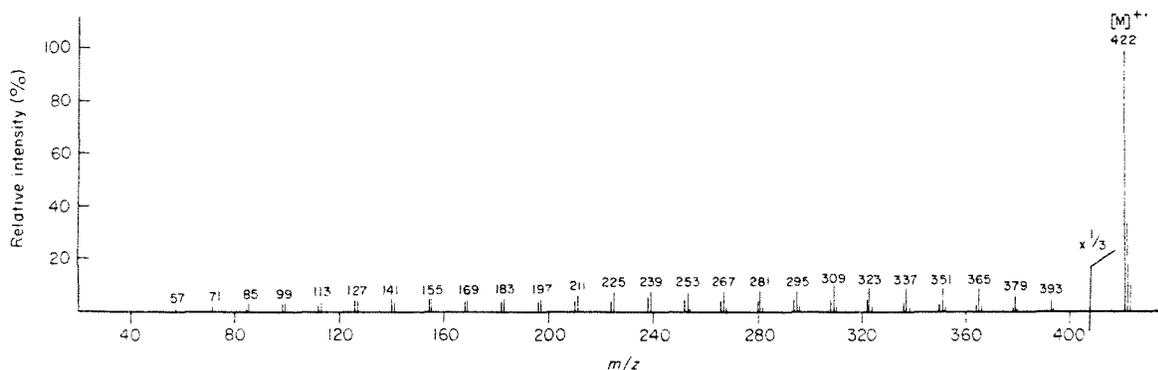
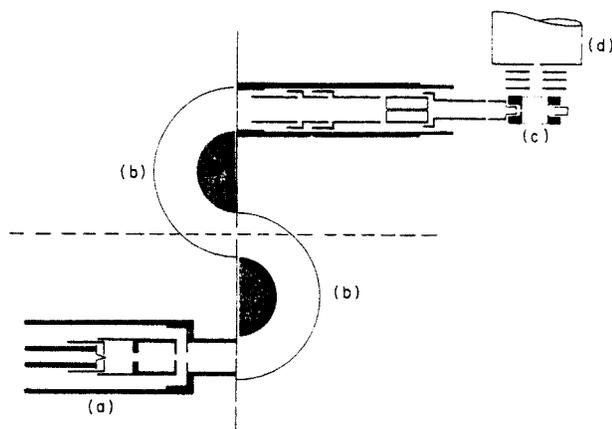
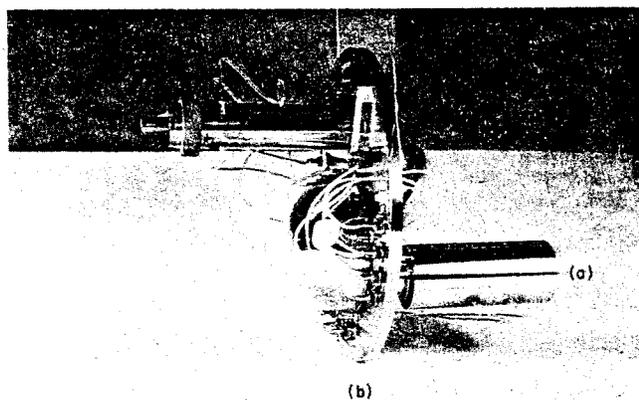
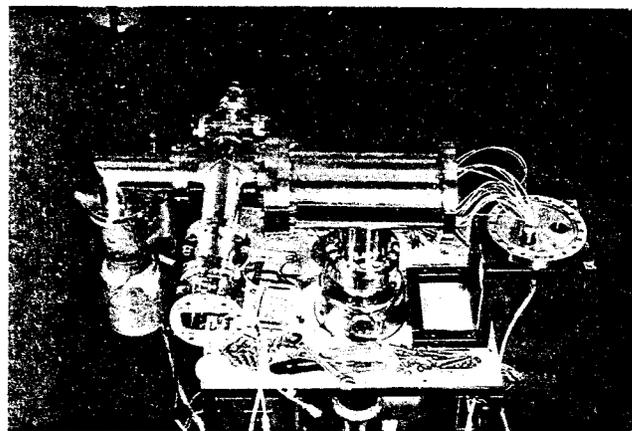
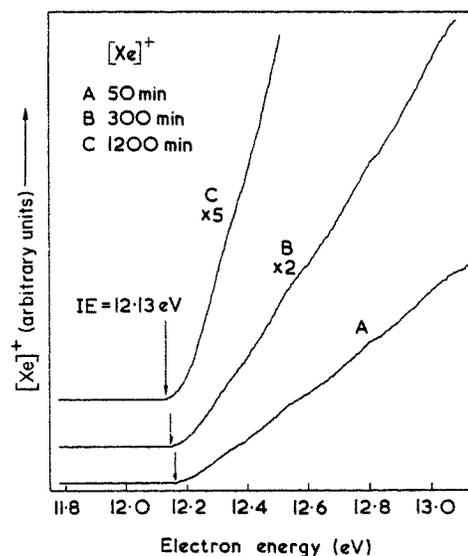


Figure 2. The mass spectrum of triacontane at 12 eV and ~350 K.

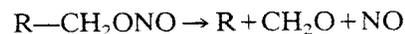
Table 1. $\Delta H_f([C_3H_5]^+)/kJ\ mol^{-1}$ from different sources

Process	$\Delta H_f([C_3H_5]^+)$
No dissociation	
$e + CH_2-\overset{\cdot}{C}H-CH_2 \rightarrow CH_2-\overset{+}{C}H-CH_2 + 2e$	946
One bond dissociation	
$e + CH_2=CH-\overset{\cdot}{C}H_2 \rightarrow [C_3H_5]^+ + H + 2e$	949
$e + CH_2=CH-\overset{\cdot}{C}H_2-CH_3 \rightarrow [C_3H_5]^+ + CH_3 + 2e$	945
Two bond dissociations	
$e + \overbrace{CH_2-\overset{\cdot}{C}H_2}^{\cdot}-CH \rightarrow [C_3H_5]^+ + H + 2e$	944
$e + \overbrace{CH_2-\overset{\cdot}{C}H_2}^{\cdot}-CH-CH_3 \rightarrow [C_3H_5]^+ + CH_3 + 2e$	945
One bond dissociation and hydrogen transfer	
$e + H-\overset{\cdot}{C}H_2-\overset{\cdot}{C}H=CH-CH_3 \rightarrow [C_3H_5]^+ + CH_3 + 2e$	943
$e + H-\overset{\cdot}{C}H_2-\overset{\cdot}{C}=CH_2 \rightarrow [C_3H_5]^+ + CH_3 + 2e$	945
Two bond dissociations and hydrogen transfer	
$e + \overbrace{CH_2-\overset{\cdot}{C}H_2-\overset{\cdot}{C}H_2}^{\cdot}-CH-H \rightarrow [C_3H_5]^+ + CH_3 + 2e$	948
Average $946\ kJ\ mol^{-1}$	


Figure 3. The electron monochromator (schematic): (a) electron gun; (b) the hemispheres; (c) the collision region; (d) the quadrupole. (N.B. The diagram should be folded through 90° along the dotted line.)

Figure 4. The hemisphere system: (a) the electron gun; (b) the hemispheres; (c) the collimator.

Figure 5. The apparatus with the end plates off the electron gun region and the quadrupole region.

Figure 6. A plot of ion count (arbitrary units) against electron energy, showing the vanishing current method.

Heats of formation

$[C_nH_{2n+1}]^+$. We can now turn to the experimental results, dealing first with carbonium ions. Lossing⁶ showed that alkyl radicals could be produced by thermolysis of alkyl nitrites.



These could then be led into the source of the monochromator and the ionization energy and hence the heat of formation of the carbonium ion determined.^{7,8} The results are shown in Table 2. It is readily seen that carbonium ion stability increases along the series

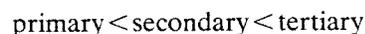


Table 2. $\Delta H_f/\text{kJ mol}^{-1}$ for alkyl ions

Primary		Secondary		Tertiary
$[\text{CH}_3]^+$	1092			
$[\text{C}_2\text{H}_5]^+$	916			
$[1-\text{C}_3\text{H}_7]^+$	870	$[2-\text{C}_3\text{H}_7]^+$	803	$[\text{tert}-\text{C}_4\text{H}_9]^+$ 699
$[1-\text{C}_4\text{H}_9]^+$	841	$[2-\text{C}_4\text{H}_9]^+$	766	
$[\text{iso}-\text{C}_4\text{H}_9]^+$	833			
$[1-\text{C}_5\text{H}_{11}]^+$	812*			
$[\text{neo}-\text{C}_5\text{H}_{11}]^+$	787	$[2-\text{C}_5\text{H}_{11}]^+$	749	$[\text{tert}-\text{C}_6\text{H}_{13}]^+$ 674
$[1-\text{C}_6\text{H}_{13}]^+$	791*	$[2-\text{C}_6\text{H}_{13}]^+$	724	$[\text{tert}-\text{C}_6\text{H}_{13}]^+$ 649
$[1-\text{C}_7\text{H}_{15}]^+$	766*	$[2-\text{C}_7\text{H}_{15}]^+$	703 ^a	$[\text{tert}-\text{C}_7\text{H}_{15}]^+$ 628

* Estimated

One further series of interest is the β -methylated series as distinct from the α -methylated series discussed above. Thus, if we compare

1-propyl 2-methyl-1-propyl 2,2-dimethyl-1-propyl
870 833 787

it is apparent that methyl substitution, one carbon removed from the charged centre is about half as effective in stabilizing the carbonium ion as is methyl substitution at the charged centre.

$[\text{C}_n\text{H}_{2n+2}\text{N}]^+$. Turning now to the ions $[\text{C}_n\text{H}_{2n+2}\text{N}]^+$, the heats of formation have been reported recently by Lossing, Lam and Maccoll.⁹ The results are shown in Table 3.

Table 3. $\Delta H_f/\text{kJ mol}^{-1}$ for the ions $[\text{C}_n\text{H}_{2n+2}\text{N}]^+$

Ion	$\Delta H_f/\text{kJ mol}^{-1}$		
$[\text{CH}_5\text{N}]^+$	$[\text{CH}_2\text{NH}_2]^+ a$ 745		
$[\text{C}_2\text{H}_6\text{N}]^+$	$[\text{CH}_3\text{CHNH}_2]^+ b$ 657		$[\text{CH}_3\text{NHCH}_2]^+ c$ 695
$[\text{C}_3\text{H}_8\text{N}]^+$	$[\text{CH}_3\text{CH}_2\text{CHNH}_2]^+ d$ 636	$[(\text{CH}_3)_2\text{CNH}_2]^+ e$ 590	$[\text{CH}_3\text{CHNHCH}_2]^+ f$ 615
	$[(\text{CH}_3)_2\text{NCH}_2]^+ g$ 661		$[\text{CH}_3\text{CH}_2\text{NHCH}_2]^+ h$ 653

Comparison of *a*, *b* and *e* shows the large effect of methylation on the carbon atom adjacent to the nitrogen, while comparison of *a*, *c* and *g* shows the smaller effect of substitution on the nitrogen.

Table 4. $\Delta H_f/\text{kJ mol}^{-1}$ for the ions $[\text{C}_n\text{H}_{2n+1}\text{O}]^+$

Ion	$\Delta H_f/\text{kJ mol}^{-1}$		
$[\text{CH}_3\text{O}]^+$	$[\text{CH}_2\text{OH}]^+ i$ 707		
$[\text{C}_2\text{H}_5\text{O}]^+$	$[\text{CH}_3\text{CHOH}]^+ j$ 582	$[\text{CH}_3\text{OCH}_2]^+ k$ 657	
$[\text{C}_3\text{H}_7\text{O}]^+$	$[\text{CH}_3\text{CH}_2\text{CHOH}]^+ l$ 552	$[\text{CH}_3\text{CHOCH}_2]^+ n$ 552	$[\text{CH}_2\text{OCH}_2\text{CH}_3]^+ o$ 607
$[\text{C}_4\text{H}_9\text{O}]^+$	$[\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)\text{OH}]^+ p$ 481	$[(\text{CH}_3)_2\text{COCH}_2]^+ q$ 477	$[\text{CH}_3\text{CHOC}_2\text{H}_5]^+ r$ 502 ^a
$[\text{C}_5\text{H}_{11}\text{O}]^+$	$[(\text{CH}_3)_2\text{COC}_2\text{H}_5]^+ s$ 435		

$[\text{C}_n\text{H}_{2n+1}\text{O}]^+$. In the case of the ions $[\text{C}_n\text{H}_{2n+1}\text{O}]^+$, Lossing's results¹⁰ are shown in Table 4. Comparison of *i*, *j* and *m* shows the high degree of stabilization due to substitution at the α -carbon atom, whereas comparison of *i* and *k*, *j* and *n* or *m* and *q* shows the much smaller effect of substitution on the oxygen. This is the same as was observed in the case of the amines, and led Lossing to propose that the structure of the oxygen ion can be written as CH_2OH and not $\text{CH}_2=\text{OH}$. The same would appear to be true for the nitrogen ions.

Estimated values. Holmes, Fingas and Lossing¹¹ have produced a scheme for estimating the heats of formation of even electron ions. They fit the results for a number of series to the formula

$$\Delta H_f([\text{M}]^+) = A - B_n + C/n \quad (5)$$

where *n* is the total number of atoms in the molecule, and the coefficients *A*, *B* and *C* are reported for each series. Excellent agreement with experiment is obtained. I will make considerable use of this valuable compilation in what follows.

PIMS No. 2

We are now in a position to apply the data that I have discussed, to an interpretation of low voltage, low temperature mass spectra.

EXPERIMENTAL

An updated MS9 spectrometer was used for this work, the only additional modification being the replacement of the electron energy voltmeter by a digital voltmeter. The cooled source was used ($\sim 350\text{ K}$) with a trap current of $10\ \mu\text{A}$. A xenon sample ($I(\text{Xe}) = 12.13\text{ eV}$) at a pressure of about 2×10^{-6} Torr was introduced through the gas inlet and the ion current normalized at 10 000 on the collector meter, at an energy of 15 eV. The electron energy was then reduced in 0.5 eV steps down to 11 eV. A plot was then made and the extrapolated value of the electron energy at onset noted. The electron energy was then set at this value and the sample spectrum run (pressure $\sim 3 \times 10^{-6}$ Torr) in the normal manner. For the purpose of counting the

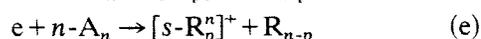
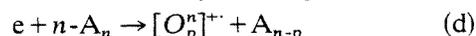
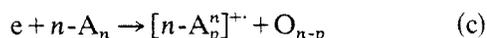
spectrum, a normal spectrum at 20 eV or 50 eV was run, overloaded if necessary. The low voltage spectrum could then be compared with the complete spectrum. Each spectrum was run three times, and the average relative abundance of the peaks calculated. If it was required to mass measure a peak, it was focused at low energy and then the energy was increased allowing mass measurement to be carried out in the normal way.

RESULTS

Consideration of PIMS No. 2 will be restricted to three classes of compounds—hydrocarbons, amines and alcohols.

Hydrocarbons

Dealing first with the hydrocarbons, three processes (c), (d) and (e) are possible,



where $n-A_n$ is the normal alkane of carbon number n , O_p^n is the alkene of carbon number p and R_p^n the radical of carbon member p produced from $n-A_n$. Figure 7 gives the EI mass spectra, while Fig. 8 shows the photoionization mass spectra of the n -alkanes from the works of Steiner, Giese and Inghram,¹² obtained at an energy of 11.25 eV, compared with the

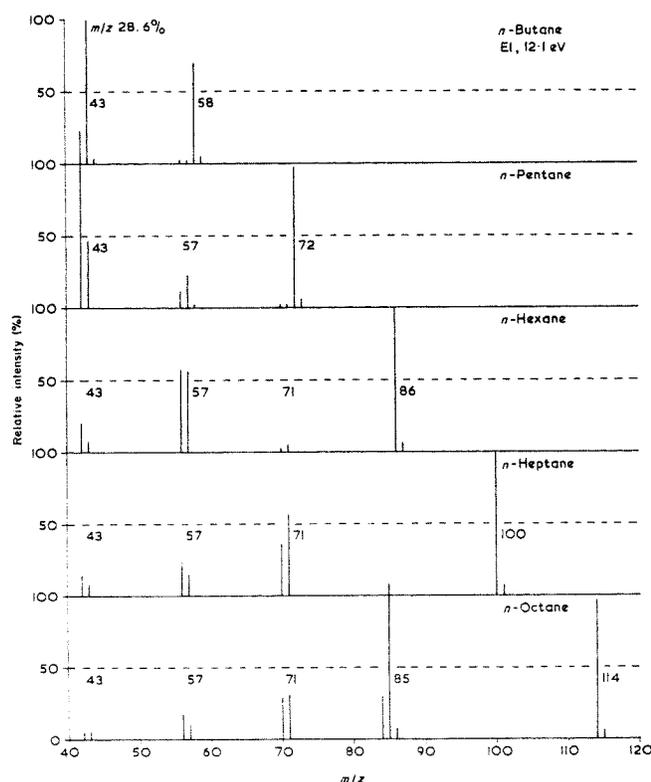


Figure 7. The low energy mass spectra of the n -alkanes. Numbers below the dotted line are the mass number of the peaks.

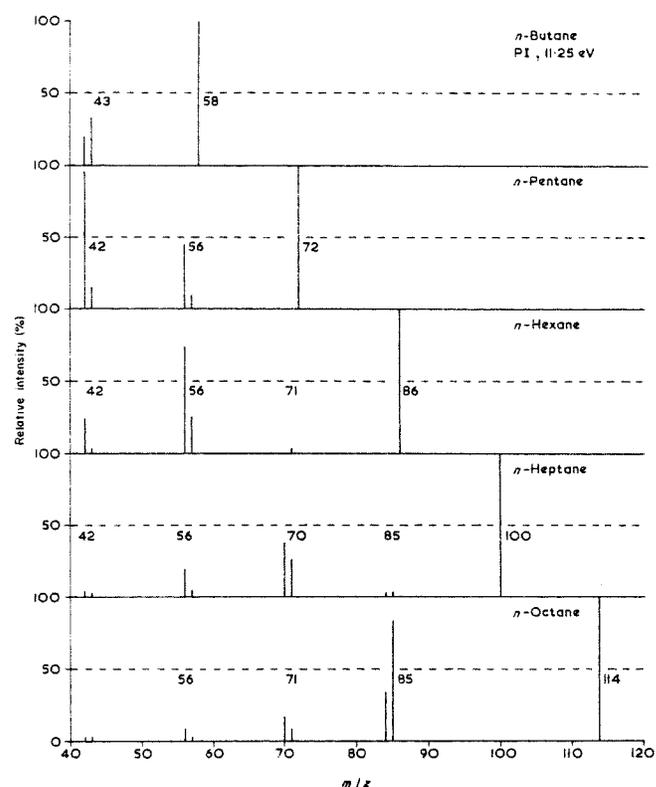
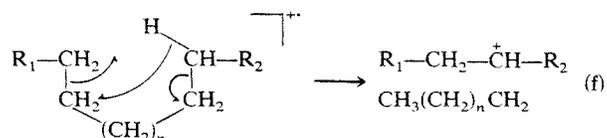


Figure 8. The photoionization mass spectra of the n -alkanes.

electron impact energy of 12.1 eV. The prominent peaks correspond to $[O]^{+\cdot}$ and $[R]^{+\cdot}$, with the former being more predominant in the photoionization studies. Using the heats of formation of $[O]^{+\cdot}$ and $[R]^{+\cdot}$ from references 7 and 9 and the neutral heats of formation from reference 9 yields the values of ΔH for the processes (c), (d) and (e). The olefin is assumed to be the 1-olefin, and the radical the secondary radical produced by process (f) as suggested by Lavanchy,



Houriet and Gaumann.¹³ Wendelboe, Bowen and Williams have recently proposed an alternative mechanism.¹⁴ Inspection of the results for a number of alkanes show that $A(R^+) < \Delta H(p-R^+)$ and so the formation of primary ions is energetically excluded. On this basis, Table 5 shows the calculated ΔH and the observed $A([A_p^n]^{+\cdot})$, $A([O_p^n]^{+\cdot})$ and $A([R_p^n]^{+\cdot})$ for n -octane.

Table 5. Calculated $\Delta H/\text{eV}$ and observed $A([O_p^n]^{+\cdot})/\text{eV}$ and $A([R_p^n]^{+\cdot})/\text{eV}$ for n -octane

m/z	100	99	98	86	85	84	72	71
ΔH	—	10.91	10.18	11.17	10.78	10.33	11.21	10.82
A	—	—	—	—	10.53	10.46	—	10.89
m/z	70	58	57	56	44	43	42	
ΔH	10.36	11.39	10.78	10.48	11.82	10.78	10.57	
A	10.74	—	11.01	10.81	—	—	—	

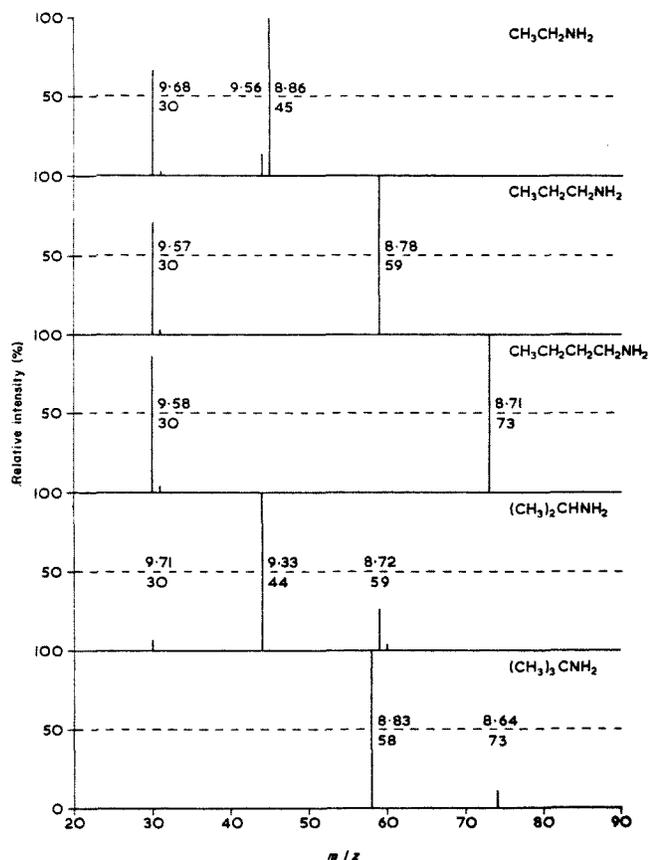


Figure 12. The low energy, low temperature mass spectra of some amines.

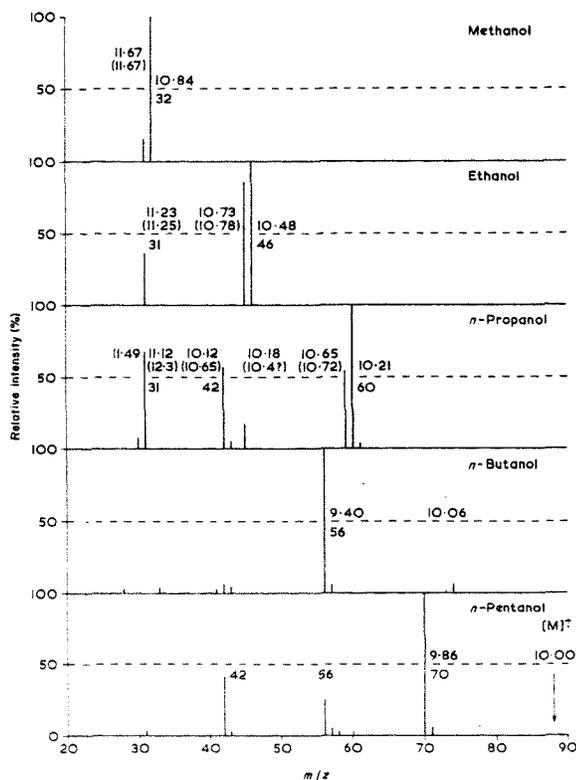


Figure 13. The low energy, low temperature mass spectra of some alcohols. Values in parentheses represent experimental values.

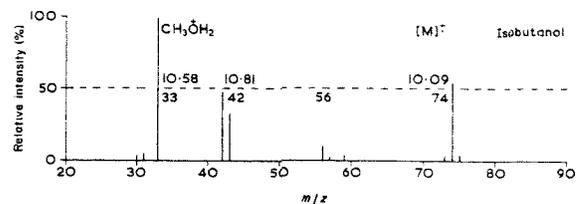
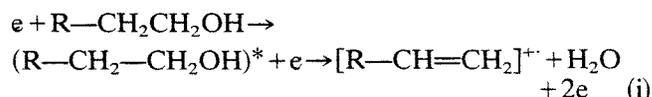
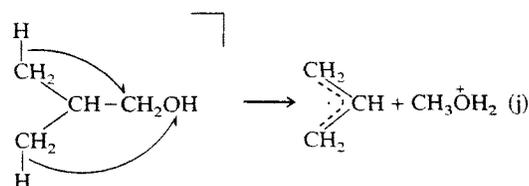


Figure 14. The low energy, low temperature mass spectra of isobutanol.

been measured by Refaey and Chupka.¹⁶ The calculated values of ΔH and the observed appearance energies are in reasonable agreement. After *n*-propanol the predominant peak is $[\text{M}-\text{H}_2\text{O}]^+$. Of considerable interest is that the ΔH for the loss of water for the last two molecules is *less than* the ionization energy, assuming the formation of the 1-olefin. This is due in the main to the large negative heat of formation of water. The suggested mechanism for the production of olefin is through the intervention of an optical metastable produced by electron impact, which then undergoes dissociation autoionization to yield the olefin ion and water.¹⁷



This suggests that the non-observation of molecular peaks for the higher alcohols arises from this phenomenon, rather than from the thermal instability of the molecular ion. The peak at m/z 33 in the mass spectrum of isobutanol, which is in fact the base peak (Fig. 14), is also of interest. That this is a low energy peak is confirmed by the proton affinity of 760 kJ mol^{-1} reported by Haney and Franklin.¹⁸ This leads to a ΔH for the process



of 10.58 eV compared with the ionization energy of 10.15 eV. This type of fragmentation is probably rather rare, depending upon the geometry of the parent ion and the stability of the fragment ion. The mechanism of this process has been discussed by Bowen and Williams.¹⁹

Finally, it is of interest to compare the effect of methyl substitution on $(\text{CH}_3)_x\text{CH}_{3-x}\text{Y}$ ($x = 1, 2, 3$; $\text{Y} = \text{CH}_3, \text{NH}_2, \text{OH}$). Figure 15 shows the case of the alkanes, propane, isobutane and neopentane taken from the photoionization spectra of Steiner *et al.* (11.25 eV). No fragmentation is observed for propane, since all possible processes have $\Delta H > 11.25 \text{ eV}$. For isobutane, the predominant peak is at m/z 42, whereas $[\text{M}-\text{CH}_3]^+$ is only $\sim 15\%$. For neopentane, $[\text{M}-\text{CH}_3]^+$ dominates the situation. In the case of the amines (electron impact, 12.1 eV), $[\text{M}-\text{CH}_3]^+$ is the base peak for isopropylamine and tert-butylamine and

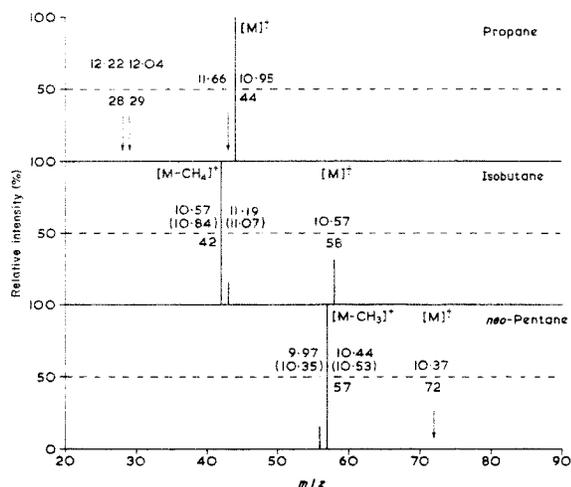


Figure 15. The photoionization mass spectra of some alkanes (after Steiner et al.¹²).

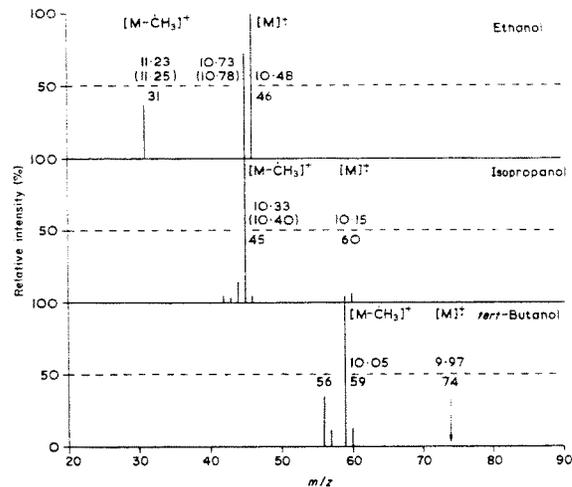


Figure 17. The low energy, low temperature mass spectra of some alcohols.

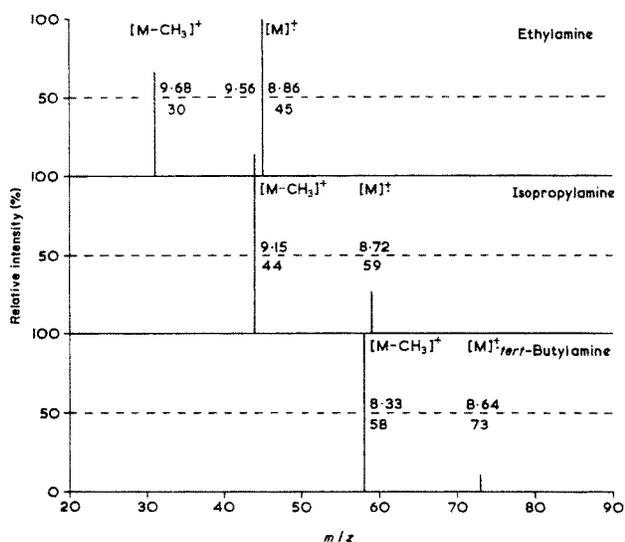


Figure 16. The low energy, low temperature mass spectra of some amines.

has a relative abundance of 65% for ethylamine (Fig. 16). The same general picture emerges for the alcohols (Fig. 17). It is of interest to note the exceptionally good agreement of ΔH and A for the fragment ions of ethanol and isopropanol.

CONCLUSION

I hope I have quoted sufficient examples to show the value of PIMS No. 2 in understanding the primary decomposition undergone by molecular ions aided by

the now established knowledge of the energetics of the processes involved. One can confidently predict that further work in this field will give evidence of new and unsuspected rearrangement processes with low energy requirements, thus adding to our knowledge of ion chemistry. One of the advantages of PIMS No. 2 is the fact that no sophisticated hardware is necessary and in fact we operate the MS9 with all slits fully open. The information obtained is comparable with that gained from photoionization experiments, a much more exacting technique and one available in only very few laboratories. Similar information can be gained from the rather sophisticated B/E scans, but these frequently involve computer control and hence may be much more expensive. In addition, it is doubtful whether the results obtained are as reliable as those obtained by the technique illustrated in this paper. Professor Beynon has said that in mass spectrometer design, the wrong choice is often made, as for example in the conventional geometry rather than reversed geometry of double sector instruments. Equally this could be said about mass spectrometer manufacturers designing their organic mass spectrometers to operate at 50–100 eV electron beam energies. Had as much effort and investment been made in producing reliable low energy electron beam instruments (10–20 eV) ion chemistry would be in a healthier state today.

Acknowledgement

I should like to acknowledge my great indebtedness to Dr F. P. Lossing whose pioneering work in the accurate evaluation of ion enthalpies has been a source of constant inspiration for me. I also wish to thank Dr M. A. Baldwin for help in the building of the monochromator and for many stimulating discussions.

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