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JMS Letters

Dear Sir,

Ion–Molecule Reactions of Ionic Species from Acetonitrile with Unsaturated Hydrocarbons for the Identification of the Double-bond Position Using an Ion Trap

In a previous paper[1] we reported on the effectiveness of acetonitrile as a reactant for the positive-ion chemical ionization (PICI) of long-chain hydrocarbons. Experiments carried out in an ion-trap-based GC–MS system showed the favoured formation of $[M + C_2H_2N]^+$ cations. The dependence on temperature of the mass spectra of long-chain hydrocarbons,[2] observed in either electron impact or classical PICI conditions[3] (i.e. employing a protonating medium such as $CH_5{}^+$ or $NH_4{}^+$), was strongly reduced under PICI(CH_3CN). Consequently, this last technique represents a particularly valuable analytical tool for the analysis of hydrocarbons.

We wish to report here further results which can give a rationale of the already described behaviour, together with new data that show the effectiveness of this approach also for the determination of the double-bond position in unsaturated long-chain hydrocarbons.

Ion-trap-based instruments represent particularly valuable devices for performing chemical ionization experiments, owing to the possibility of choosing both the most appropriate reactant species and reaction times.

The spectrum obtained upon introduction of acetonitrile into the ion trap of a Saturn 2000 GC–MS (Varian, Walnut Creek, CA, USA) with ionization time 2 ms, reaction time 100 ms, manifold temperature 150 °C and helium buffer pressure 3×10^{-5} Torr is mainly due to four ionic species: while the odd-electron molecular ion of acetonitrile at *m/z* 41 is of low abundance (26%), most of the total ion current is due to the protonated molecule $[C_2H_4N]^+$ (*m/z* 42, 100%), to the $[M - H]^+$ cation (*m/z* 40, 41%) and to an ionic species at *m/z* 54 (21%) corresponding to the elemental formula C_3H_4N. Consequently, one could expect acetonitrile to act as a protonating medium. However, thermodynamic data, in particular proton affinity (PA) values, indicate that acetonitrile exhibits a PA (792.9 kJ mol^{-1})[4a] higher than those of hydrocarbons (e.g. $PA_{butane} = 697.9$ kJ mol^{-1}, $PA_{butene} = 761.1$ kJ mol^{-1})[4b] and hence $[M + H]^+$ ions of acetonitrile cannot be considered as a protonating species for hydrocarbons.

The data reported previously[1] showed that among the ionic species mentioned above, those at *m/z* 40 are highly reactive against hydrocarbons. Saturated hydrocarbons up to C_{37}, when reacted with the ion set just discussed, give rise to $[M + 40]^+$ species, whose abundance shows a clear increase with increasing chain length. The only fragments observed correspond to losses, from the $[M + 40]^+$ species, of alkenes of different length (see Fig. 1 as an example), in agreement with the even-electron rule.[5]

In the case of saturated hydrocarbons, ionic species $[M + 54]^+$ have never been observed, thus proving that the only ionic species reactive against saturated hydrocarbons are $[C_2H_2N]^+$ cations.

Many different structures can be considered for the species at *m/z* 40, such as structures **a**–**h** given overleaf.

In our opinion, structures **a** and **c** represent the most reasonable ones. The observed alkene losses seem to suggest that the addition of **a** or **c** species could take place on the terminal part of the hydrocarbon chain, probably on the C atom in position 2. Work is in progress to investigate the detailed mechanism(s) of the addition of $[C_2H_2N]^+$ by theoretical calculations and labelling experiments.

In the case of mono-unsaturated hydrocarbons, some peculiar behaviours are evidenced. As an example, the mass spectra of (9)C23 : 1 and (7)C23 : 1 are reported in Fig. 2. In these cases, together with $[M + 40]^+$ ions at *m/z* 362, a new reaction product is detected at *m/z* 356 corresponding to $[M + 54]^+$, i.e. the addition product of the species at *m/z* on the hydrocarbon. The same behaviour has been observed for other mono-unsaturated hydrocarbons (see Table 1) of natural

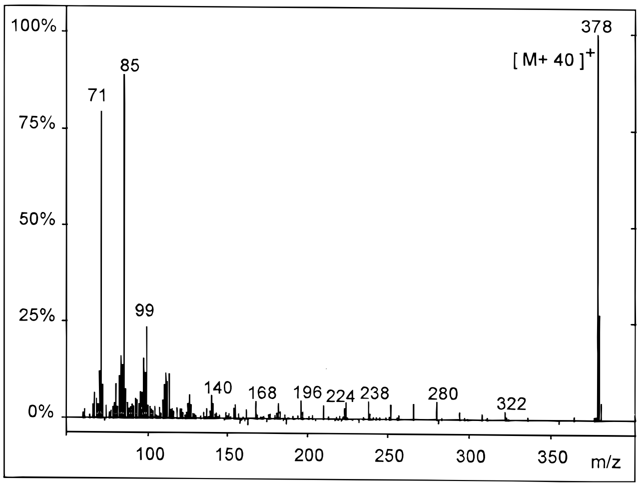

Figure 1. PICI(CH_3CN) mass spectra of C24.

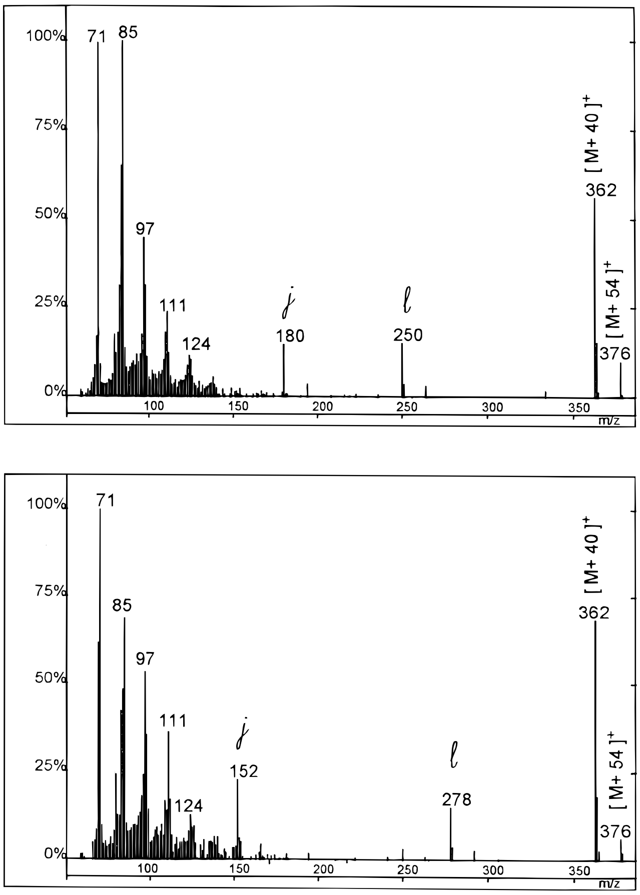

Figure 2. PICI(CH_3CN) mass spectra of mono-unsaturated hydrocarbons (9)C23 : 1 (top) and (7)C23 : 1 (bottom).

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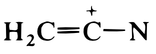
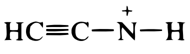
$H_2C{=}C{=}N^+$

a



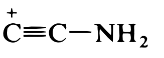
$H_2C{=}\overset{+}{C}{-}N$

b



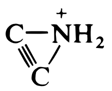
$HC{\equiv}C{-}\overset{+}{N}{-}H$

c

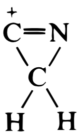


$\overset{+}{C}{\equiv}C{-}NH_2$

d



e



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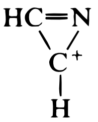
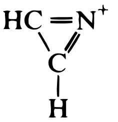


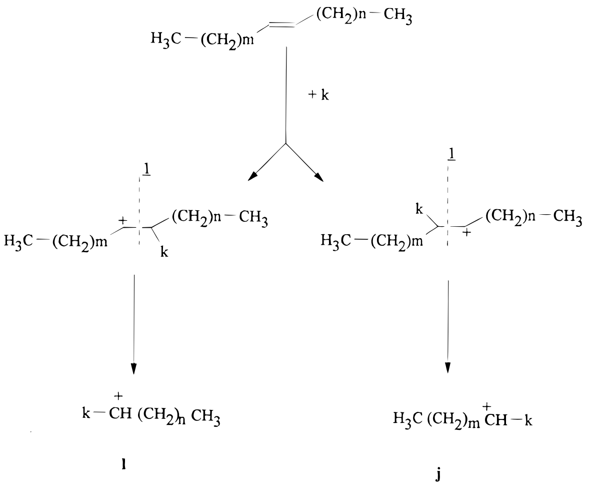
g



h

Table 1. Relative abundances (RA) of ionic species $[M+40]^+$ and $[M+54]^+$ observed in PICI(CH_3CN) spectra of mono-unsaturated hydrocarbons

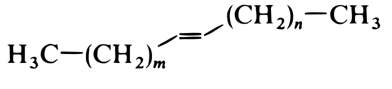
Hydrocarbon		$[M+40]^+$		$[M+54]^+$	
Formula	Double-bond position	*m/z*	RA	*m/z*	RA
C15:1	7	250	2	264	3.5
C23:1	9	362	41	376	11
C23:1	7	362	37	376	5
C25:1	9	390	54	404	14
C25:1	7	390	48	404	11



Scheme 1.

Table 2. *m/z* values and relative abundances (RA) of ionic species j and l (see Scheme 1) observed in PICI(CH_3CN) spectra of mono-unsaturated hydrocarbons, diagnostically relevant for determination of double-bond position

Hydrocarbon			Species (j)		Species (l)	
Formula	Double-bond position	*m, n*	*m/z*	RA	*m/z*	RA
C15:1	7	5, 6	152	4	166	6
C23:1	9	7, 12	180	10	250	10
C23:1	7	5, 14	152	23	278	19
C25:1	9	7, 14	180	13	278	12
C25:1	7	5, 16	152	11	306	10



origin, present in natural extracts of wasps[6] (*Parischnogaster striatula* and *Parischnogaster alternata*; venom gland and Dufour gland). Their structural assignment has been performed by alkylthiolation using the procedure of Francis and Veland,[7] followed by EI mass spectrometry.

Hence by PICI(CH_3CN) an easy characterization of hydrocarbon mixtures can be achieved: the saturated compounds lead to $[M + 40]^+$ species only, while the mono-unsaturated ones give rise to both $[M + 40]^+$ and $[M + 54]^+$ cations. Furthermore, a deeper examination of the PICI spectra of unsaturated hydrocarbons evidences a behaviour highly relevant from the analytical point of view. The spectra reported in Fig. 2 show the presence of pairs of peaks of quite high abundance [*m/z* 180 and 250 for (9)C23:1; *m/z* 152 and 278 for (7)C23:1] which do not relate to the fragment series originated by the alkene losses discussed above for saturated hydrocarbons. They can be easily justified by the occurrence of the pathways shown in Scheme 1. The reactive species at *m/z* 54 (**k**) can add to both CH groups of the double bond: by further cleavage of the addition products, species **j** and **l** are easily formed. This behaviour has been observed for all the compounds under investigation and the related data are summarized in Table 2.

The above results provide good evidence that by reaction of PICI-generated acetonitrile species on hydrocarbons, both the identification of the molecular weight and the position of the double bond in mono-unsaturated derivatives can be unequivocally obtained.

Yours,

GLORIANO MONETI,[1]* GIUSEPPE PIERACCINI,[1] FRANCESCA DANI,[2] STEFANO TURILLAZZI,[3] DONATA FAVRETTO[4] and PIETRO TRALDI[5]

[1] Centro Interdipartimentale di Servizi
di Spettrometria di Massa,
Universitá di Firenze,
Via G. B. Morgagni 65,
I-50134 Firenze, Italy
[2] Department of Chemistry,
University of Keele,
Keele, Staff, UK
[3] Dipartimento di Biologia Animale e Genetica,
Universitá di Firenze,
Via Romana 17,
I-50125 Firenze, Italy
[4] CNR, Area della Ricerca,
Corso Stati Uniti 4,
I-35100 Padova, Italy
[5] CNR, Centro di Studio sulla Stabilitá
e Reattivitá dei Composti di Coordinazione,
Via Marzolo 1,
I-35100 Padova, Italy

* *Correspondence to*: G. Moneti, Centro Interdipartimentale di Servizi di Spettrometria di Massa, Universitá di Firenze, Via G. B. Morgagni, I-50134 Firenze, Italy

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