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Effect of ion source pressure on ion formation of carbamates in particle-beam chemical-ionisation mass spectrometry

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Abstract

In this study the mass spectra of fourteen carbamate pesticides, obtained with desorption chemical ionisation (DCI) and flow injection (FIA)–particle beam (PB)-ammonia positive chemical ionisation (PCI)-mass spectrometry (MS), are compared. The mass spectra from the FIA–PB-PCI-MS experiments exhibit higher relative abundances for fragment ions. The influence of the ion source pressure and temperature on the ion abundances under ammonia positive chemical ionisation conditions was studied. The results indicate that thermal degradation of the carbamate pesticides takes place in the FIA–PB-MS system. In addition, the $[M + NH_3 + H]^+$ and $[M + NH_3 + H - CH_3NCO]^+$ ion intensities are strongly dependent on the ion source pressure, especially for carbofuran as an extreme. Both the ion source pressure and the temperature cause irreproducibility of the ammonia PCI mass spectra of carbamates under liquid chromatography PB-PCI-MS conditions and it is therefore of utmost importance to use well defined experimental conditions for the quantitative determination of carbamates.

1. Introduction

Under conventional conditions, the gas chromatographic (GC) quantitation of carbamates and some of their transformation products is rather unreliable, because thermal degradation may occur. Nevertheless, it has been shown that GC with electron ionisation mass spectrometric detection (GC–EI-MS) generally leads to irrefutable identification of the compounds [1,2]. Recently, it was observed that GC with positive chemical ionisation (PCI)-MS detection, using methane as the reagent gas, results in a better sensitivity of detection by a factor of 2 for carbofuran and carbaryl [3]. Similarly, in a previous study, the use of ammonia as a reagent gas [4] resulted in a 3–7 times lower limit of detection for these carbamates. Therefore, PCI–MS with ammonia may be expected to generally provide the lower limits of detection. In addition, specific fragmentation of the most widely used N-methylcarbamates under PCI conditions, in particular the loss of methylisocyanate (CH_3NCO) from the protonated molecule, provides some structural confirmation. Thus, GC with ammonia PCI-MS detection would provide an ideal method for carbamate analysis if the problem of thermal degradation could be circumvented.

Several modified GC procedures have been

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developed to prevent thermal decomposition: reducing the analysis time by using shorter columns [5,6], application of programmed temperature vaporisation (PTV) injection [7], and the use of special types of stationary phases [8]. However, these procedures have not led to analytical methods that are generally applicable to carbamates. Moreover, transformation products of carbamates, which tend to be even more polar, cannot be determined by GC–MS without prior derivatisation. The application of liquid chromatography (LC) is to be preferred, because of both the lack of thermal decomposition during separation and the additional possibility to simultaneously analyse the transformation products.

Various liquid chromatographic–mass spectrometric (LC–MS) interfacing methods have been applied in the determination of carbamates and their transformation products, e.g. direct liquid introduction (DLI) [9,10], thermospray (TSP) [11–16], electrospray (ESP) [17,18], atmospheric pressure chemical ionisation (APCI) [19,20] and particle beam (PB) [20–26]. In general, carbamates can be detected with all these methods with good sensitivity, i.e. typically in the low ng range. However, LC–PB-MS is to be preferred for the confirmation of carbamates in real samples [27] because it can provide solvent-independent CI and electron ionisation (EI) mass spectra.

In the PB interface the column effluent is pneumatically nebulised in a heated desolvation chamber at nearly atmospheric pressure. The solutes are selectively separated from the solvent vapour molecules in a two-stage momentum separator and subsequently transported into the ion source. It was postulated that the particles evaporate upon collision with the heated ion source wall and that the released molecules may become ionised [28]. Unfortunately, high limits of detection and non-linear calibration curves at low concentrations [20,24,25] are encountered with the PB interface. Many parameters, e.g. ion source temperature and alignment of the nebuliser, have to be optimised [29]. Moreover, the design of the nebuliser is important for the stability of the signal [23]. In a recent review all the aspects of this interface were discussed [30].

The use of LC–PB–MS for the detection of carbamates and their transformation products requires a systematic approach. It has, for example, been observed that thermal degradation of chlorophenoxy acetic acid pesticides occurs in PB-MS [31]; given the above-mentioned experience with GC, thermal degradation may also occur with the N-methyl carbamates. Moreover, differences between the methane CI mass spectra with either GC or direct inlet systems (desorption chemical ionisation, DCI) have been reported for aldicarb, butocarboxim and their oxime and nitrile derivatives [32,33]; these differences were explained to be due to thermal processes in the GC column. In order to gain insight in the applicability of LC–PB-PCI-MS to carbamate analysis, we studied the effects of various parameters on the ion formation of carbamate pesticides in flow injection (FIA)–PB-PCI-MS, by comparing the mass spectra of selected carbamate pesticides in both positive ion DCI and FIA–PB-PCI-MS experiments, using ammonia as the reagent gas.

2. Experimental

2.1. Chemicals

All carbamate pesticides, including aldicarbsulphone, were obtained from Riedel–de Haën (Seelze, Germany), the EPA (Research Triangle Park, NC, USA) or from Dr. Ehrenstorfer (Augsburg, Germany). These compounds were of 96–99 + % purity, and were used as received. Standard solutions (20 mg/l) of all carbamates were made in methanol and were stored, for a maximum of 1 year, in the dark at −20°C.

Acetonitrile (99.9% purity) was obtained from Westburg (Leusden, Netherlands). HPLC-grade water, methanol and ammonium acetate (min. 97%) were purchased from Baker (Deventer, Netherlands). All eluents were purged with helium for at least 1 h, before starting an analysis. Helium gas for the particle beam interface and methane and ammonia reagent gases,

all with a purity of 99.99%, were obtained from Hoekloos (Schiedam, Netherlands).

2.2. Mass spectrometry

Particle beam experiments were performed with a HP Model 5988A quadrupole ("MS Engine") mass spectrometer (Hewlett-Packard, Palo Alto, CA, USA) coupled with a Model 1090 Series II liquid chromatograph (Hewlett-Packard, Waldbronn, Germany). The latter was equipped with an autosampler, and interfaced to the mass spectrometer by a Model 59980A particle beam interface.

The temperature of the desolvation chamber and the analyser were maintained at 100°C. Pressure dependencies were recorded at source temperatures of 125, 175 and 225°C; a source temperature of 125°C was used for all other PB-MS experiments. Full scan spectra were acquired from m/z 85 to 350 in the PCI mode at (2.4 s/scan).

Desorption chemical ionisation mass spectra were obtained with a Finnigan MAT 90 mass spectrometer (Finnigan MAT, Bremen, Germany), using the standard direct inlet (DI) probe. Samples were introduced over a longer period of time, with the probe temperature not exceeding 60°C. Ionisation was performed with 150 eV electrons at an emission current of 0.2 mA and using ammonia as the reagent gas (at an indicated source pressure of $4 \cdot 10^{-4}$ Torr). The pressure dependence was recorded at ion source temperatures of 115, 170 and 210°C; a source temperature of 125°C was used for all other DCI experiments. Metastable ion kinetic energy (MIKE) mass spectra of $[M+H]^+$ and $[M+NH_3+H]^+$ were obtained.

2.3. Pressure measurement

Pressure measurement was performed with the available gauges; unfortunately the pressure values cannot be mutually compared. The MAT 90 source pressure is measured by an ionisation gauge, inserted in a side tube of the source manifold. The MS Engine source pressure can be read as a fore vacuum pressure, as it is measured by a cold cathode manometer. Fig. 1 gives a schematic representation of the PB and the CI ion source; the fore vacuum ("auxiliary") pressure is measured at the CI gas inlet (indicated by the arrow "CI reagent gas"). An auxiliary pressure of approximately 0.6 Torr corresponds to a source manifold pressure (measured above the inlet of the roughing pump) of $1 \cdot 10^{-4}$ Torr.

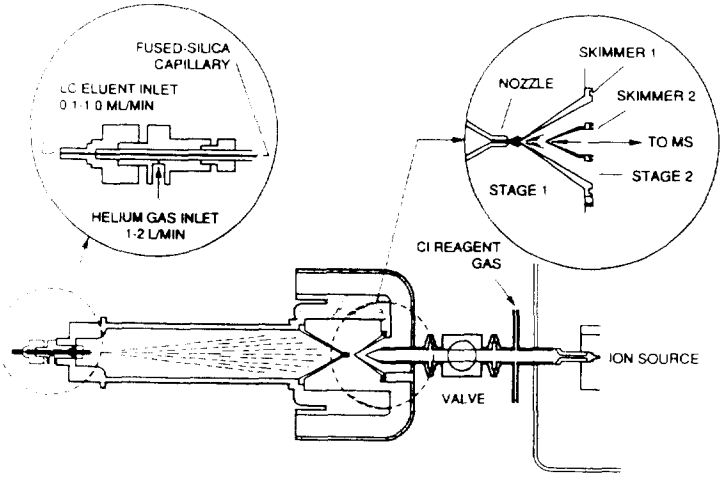

Fig. 1. Schematic representation of the particle beam interface and ion source of the MS Engine.

3. Results and discussion

Fourteen carbamates (including the transformation product aldicarbsulphone) were selected to represent the various subclasses. Mass spectra of these selected carbamates were obtained at an ion source temperature of 125°C and with ammonia as the reagent gas, using both positive ion DCI and PB-PCI; these spectra are summarised in Table 1. More fragmentation appears to occur under PB-PCI than under DCI conditions. As was reported before for TSP [15], an increase of the relative abundance of the specific fragment ion of the N-methyl carbamates, $[M+H-CH_3NCO]^+$, is related to their thermal degradation, prior to ionisation. The concomitant ion signal increase is generally masked in the EI mode, because the intensity of the molecular ion peak is 50 to 100 times lower than that of the $[M-CH_3NCO]^{+\bullet}$ ion peak; hence, an increase in the thermolysis of molecules will only result in a small contribution to the $[M-CH_3NCO]^{+\bullet}$ signal. That $[M-CH_3NCO]^{+\bullet}$ and $[M+H-CH_3NCO]^+$ are indeed formed by fragmentation of $M^{+\bullet}$ and $[M+H]^+$ ions, respectively, has been shown by metastable ion studies using deuterated methane as the reagent gas [34,35]. Thus, the $[M-CH_3NCO]^{+\bullet}$ signal, in EI, and the $[M+H-CH_3NCO]^+$ signal, in PCI, result from ionic fragmentation and from ionisation of the thermolysis product.

Under conditions of ammonia PCI the situation becomes even more complicated, because ammonia adduct ions, $[M+NH_3+H]^+$, may be generated. This gives rise to the formation of $[M+NH_3+H-CH_3NCO]^+$, either from fragmentation or from adduct ion formation of the thermolysis product. Metastable ion (MIKE) spectra were recorded from $[M+NH_3+H]^+$, as generated under DCI conditions, confirm that CH_3NCO is lost from the adduct ions, albeit that the intensity is only 1–5% of the ammonia loss. An additional problem was especially distinct in the case of carbofuran: a dramatic pressure dependence was observed under ammonia DCI conditions. Although pressure dependence in CI has been reported before and is considered a general characteristic of the method [36], the pressure dependence is only rarely problematic in the pressure regimes used for DCI and PB-CI. In the case of carbofuran, however, the relative abundances of the $[M+H]^+$ ion, the specific fragment ion, $[M+H-CH_3NCO]^+$, and their ammonia adduct ions, at m/z, 222, 165, 239 and 182, respectively, change completely between manifold pressures of $4\cdot10^{-5}$ to $4\cdot10^{-4}$ Torr. This dependence is depicted in Fig. 2, where the relative abundances of m/z 222 and 239 are plotted against the manifold pressure at three different source temperatures: 115, 170 and 210°C. The ammonium adduct ion, $[M+NH_3+H]^+$, is seen to dominate the spectrum at higher ion source pressures, but the adduct ion abundance decreases with increasing ion source temperature. The formation of the ammonium adduct ions results in the suppression of the fragment ion, $[M+H-CH_3NCO]^+$, at m/z 165. At the higher ion source temperatures the relative abundances of $[M+H]^+$, m/z 222, and $[M+NH_3+H]^+$, m/z 239, are less sensitive to pressure changes than at 115°C. Such a strong dependence of the mass spectra upon the ion source pressure is shown by none of the other carbamates studied here; intensity ratio differences may be as high as 20–30%.

The possible origin of ion signals in the ammonia PCI mass spectra of carbamates is depicted in Fig. 3. Note that the ammonium adduct ions, $[M+NH_3+H]^+$, are formally reaction intermediates in the protonation process. For example, a change in the intensity of the $[M+H-CH_3NCO]^+$ ion may be due to more or less thermolysis (process T), to the deposition of more or less energy in the product ions (in the processes A and F) or to a more or less efficient formation of the ammonium adduct ion (process A). Under ammonia PCI conditions and using either DCI or PB-CI, it is not possible to distinguish between the contributions of the various processes to the spectrum abundances of thermally labile compounds. However, it is clear that quantitation in ammonia PCI might be difficult, especially when selected-ion monitoring is used.

In order to study the effect of source pressure and temperature on ion abundances in FIA–PB-

Table 1
Main ions and their relative abundances of fourteen carbamates, obtained with ammonia PCI at an ion source temperature of 125°C and using direct probe or particle beam inlet (at $5 \cdot 10^{-4}$ Torr and 0.6 Torr indicated source pressure, respectively)

Compound Ion composition	*m/z*	Relative intensity (%)	
		DCI	PB-PCI
Aldicarb Sulphone			
$[M + H + NH_3]^+$	240	100	–
$[M + H]^+$	223	1	1
$[M + H - CH_3NCO + NH_3]$	183	10	–
$[M + H - CH_3NHCOOH + NH_3]^+$	165	8	100
Aminocarb			
$[M + H]^+$	209	100	33
$[M + H - CH_3NCO]$	152	10	100
Asulam			
$[M + H + NH_3]^+$	248	100	32
$[M + H + NH_3 - CH_3OH]$	216		45
$[M + H - 58]^+$	190	2	100
Barban			
$[M + H + (NH_3)_2]^+$	292	13	–
$[M + H + NH_3]^+$	275	100	67
$[M + H]^+$	258	1	–
$[M + H - HCl + NH_3]^+$	239	1	56
$[M + H - HCl]^+$	222	1	24
$[ClC_6H_4NCO]^+$	153		100
Bromocarbamate			
$[M + H + (NH_3)_2]^+$	292	10	–
$[M + H + NH_3]^+$	275	100	100
$[M + H]^+$	258	1	25
Carbaryl			
$[M + H + NH_3]^+$	219	100	100
$[M + H]^+$	202	2	16
$[M + H - CH_3NCO + NH_3]$	162	29	16
$[M + H - CH_3NCO]^+$	145	6	18
Carbendazim			
$[M + H + NH_3]^+$	209	4	–
$[M + H]^+$	192	100	100
Carbofuran			
$[M + H + NH_3]^+$	239	100	25
$[M + H]^+$	222	3	53
$[M + H - CH_3NCO + NH_3]$	182	13	100
$[M + H - CH_3NCO]^+$	165		23
Dioxacarb			
$[M + H + NH_3]^+$	241	100	20
$[M + H]^+$	224	2	15
$[M + H - CH_3NCO]^+$	167	21	100

(*Continued on p. 26*)

Table 1. (*Continued*)

Compound Ion composition	*m/z*	Relative intensity (%)	
		DCI	PB-PCI
Desmedipham			
$[(M - C_6H_5NCO)_2 + H + NH_3]^+$	380	3	–
$[M + H + NH_3]^+$	318	2	–
$[M + H + (NH_3)_2 - C_6H_5NCO]^+$	216	13	–
$[M + H + NH_3 - C_6H_5NCO]^+$	199	100	100
$[M + H - C_6H_5NCO]^+$	182	1	33
Ethiofencarb			
$[M + H + NH_3]^+$	243	100	100
$[M + H]^+$	226	2	32
$[M + H - CH_3NCO + NH_3]^+$	186	8	–
$[M + H - CH_3NCO]^+$	169	5	85
Pirimicarb			
$[M + H]^+$	239	100	100
Promecarb			
$[M + H + NH_3]^+$	225	100	100
$[M + H]^+$	208	1	48
$[M + H - CH_3NCO + NH_3]^+$	168	4	–
$[M + H - CH_3NCO]^+$	151	3	39
Propoxur			
$[M + H + NH_3]^+$	227	100	100
$[M + H]^+$	210	47	95
$[M + H - CH_3NCO + NH_3]^+$	170	14	–

PCI-MS five representative carbamates were selected, of which the structures are depicted in Fig. 4. The N-methylcarbamates carbofuran, dioxacarb and carbaryl were selected, because they primarily form ammonium adduct ions; in addition, we suspected dioxacarb to be extremely thermally labile because of the relatively high abundance of $[M + H - CH_3NCO]^+$ ions observed in preliminary measurements. The N-methylcarbamate aminocarb and the N,N-dimethylcarbamate pirimicarb were selected, because they show no ammonium adduct ions in their mass spectra; we suspected aminocarb to be thermolabile (on the same grounds as given above for dioxacarb), whereas pirimicarb cannot eliminate an isocyanate-type molecule and must be thermally stable. The pressure dependence of the intensity of $[M + H]^+$, $[M + NH_3 + H]^+$, $[M + H - CH_3NCO]^+$ and $[M + NH_3 + H - CH_3NCO]^+$ ions (if present) was recorded at three different source temperatures, using FIA–PB-PCI-MS with ammonia; the results are briefly discussed below.

The pressure dependencies of the ion intensities for carbofuran are depicted in Fig. 5. The behaviour of carbofuran parallels that observed in the DCI experiments. At higher temperatures the fragment ion at *m/z* 165 becomes the base peak. In addition one should note the decline of all ion intensities at higher pressures; a similar decline is not observed in the DCI experiments.

The results for dioxacarb are given in Fig. 6. The $[M + H - CH_3NCO]^+$ ion, *m/z* 167, yields the base peak already at 125°C. At a source temperature of 125°C the intensity of the ammonia adduct ions, *m/z* 184 and 241, and of the protonated molecule, *m/z* 224, increases with the ion source pressure. At higher source tem-

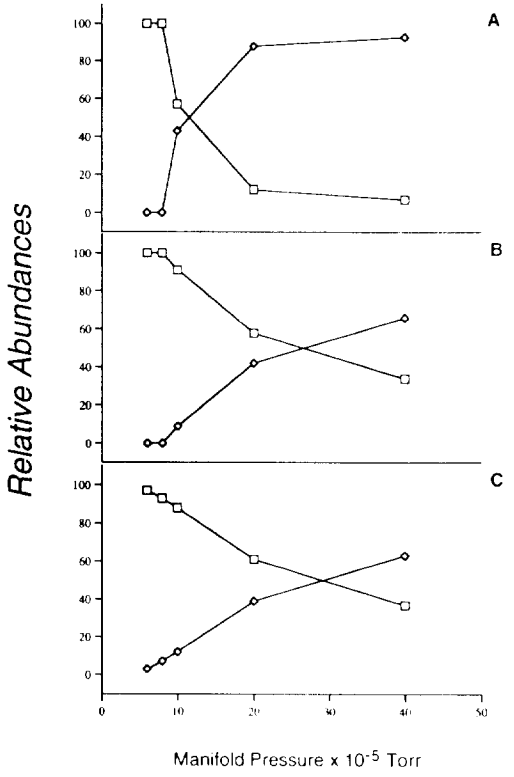

Fig. 2. Abundance of ions m/z 222 (□) and 239 (○), of carbofuran obtained from DCI experiments at different reagent gas pressures, at an ion source temperature of 115 (A), 170 (B) and 210°C (C), respectively.

perature the adduct ions, nor $[M + H]^+$ ions are observed; almost only m/z 167 remains at an ion source temperature of 225°C.

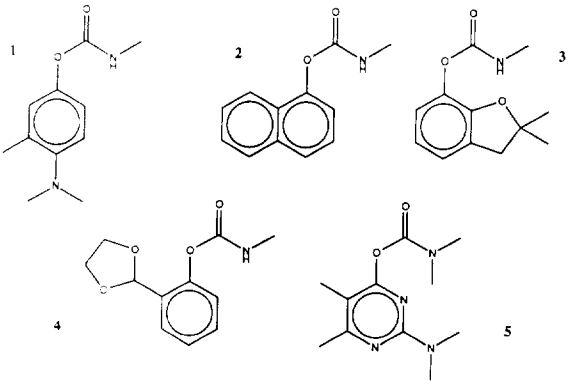

Fig. 4. Structures of the carbamate pesticides aminocarb (1), carbaryl (2), carbofuran (3), dioxacarb (4) and pirimicarb (5).

As regards carbaryl (not shown), the relative abundances of the ammonium adduct ions, m/z 162 and 219, and of $[M + H]^+$, m/z 202, increase when the ion source pressure is raised. In contrast to carbofuran, the ammonium adduct of the fragment ion, m/z 162, is not as abundant and at higher ion source temperatures the relative abundances of the ions with m/z 162, 202 and 219 do not decrease. Hence, the influence of pressure or temperature change on the PCI spectra of carbaryl is much less pronounced than with carbofuran or dioxacarb.

In analogy to observations on the TSP and DCI spectra of aminocarb (data not shown), the PB mass spectra only display $[M + H]^+$ ions, m/z

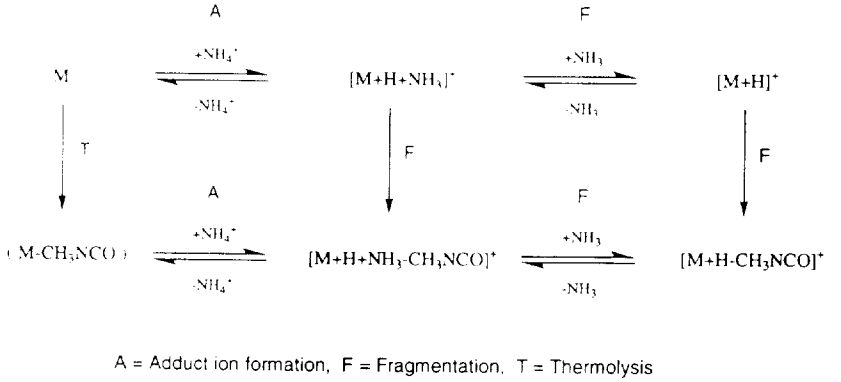

Fig. 3. Possible origin of ion signals in the ammonia PCI mass spectra of carbamates.

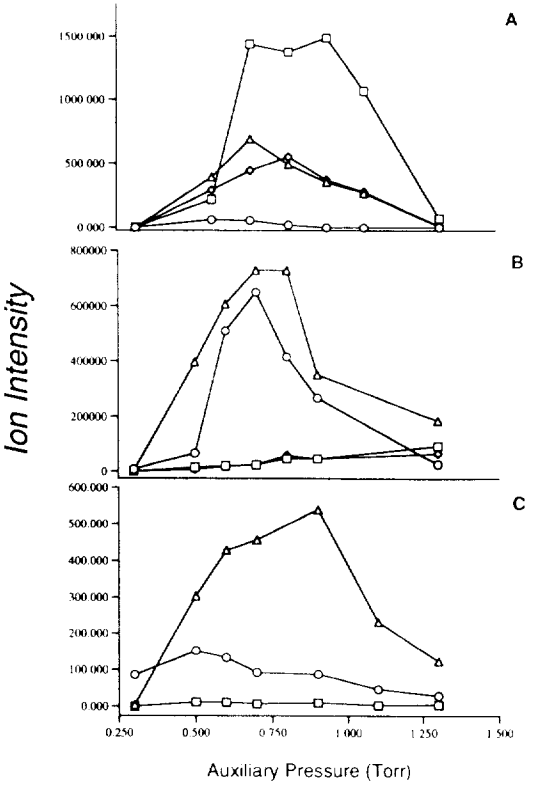

Fig. 5. Ion intensities of ions m/z 165 (○), 182 (△), 222 (□) and 239 (◇) of carbofuran at different reagent gas pressures, and at ion source temperatures of 125 (A), 175 (B) and 225°C (C).

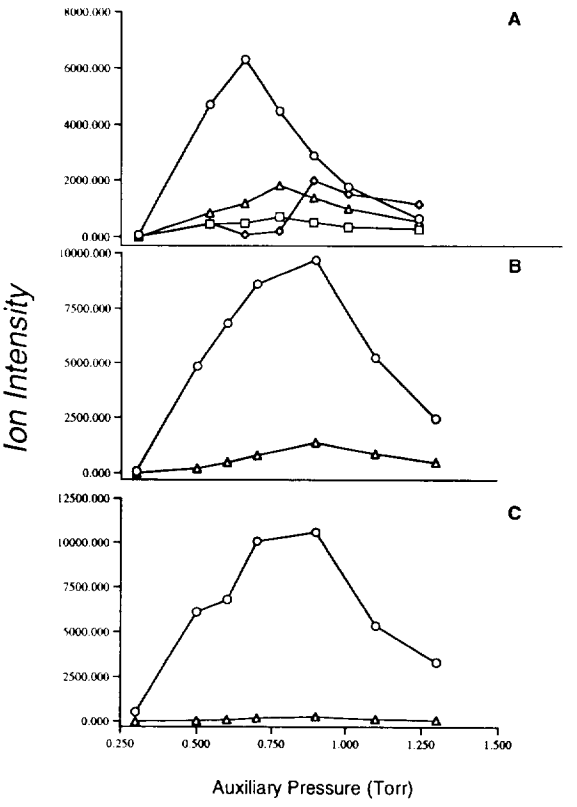

Fig. 6. Ion abundances of ions m/z 167 (○), 184 (△), 224 (□), and 241 (◇) of dioxacarb at different reagent gas pressures, and at ion source temperatures of 125 (A), 175 (B) and 225°C (C).

209, and $[M + H - CH_3NCO]^+$ ions, m/z 152. At an ion source temperature of 125°C the protonated molecule is the base peak. At higher temperatures the $[M + H - CH_3NCO]^+$ ion becomes the base peak: at 225°C the relative intensity of the protonated molecule is even decreased to less than 10% of the m/z 152 base peak. This is due to the thermal degradation of the compound in the ion source, as was mainly observed for dioxacarb (see above).

The results for pirimicarb are given in Fig. 7. The protonated molecule, m/z 239, provides the base peak at all pressures and temperatures used. Although we considered this compound to be thermally stable, the ion with m/z 166, which appears at higher source temperatures, shows that pirimicarb can lose dimethylformamide, $(CH_3)_2NC(O)H$. Because we also observe m/z 166 ions in the MIKE spectra of protonated pirimicarb obtained under ammonia DCI conditions, this fragment may arise through stimulated fragmentation of $[M + H]^+$ or through thermolysis of neutral pirimicarb. Thus, even pirimicarb may give problems in quantitation via PCI experiments.

All base peaks of the compounds tested in PB-PCI-MS show an optimum in their intensity between an indicated ion source pressure of 0.6 and 0.8 Torr, at all temperatures applied. This is in the same order of magnitude as results from earlier reports, where an optimum ion source pressure of approximately 0.4 Torr for methane

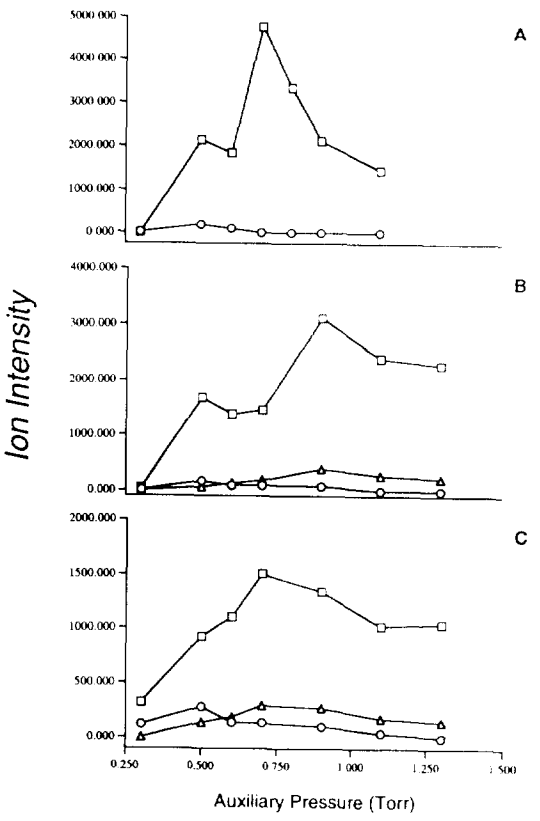

Fig. 7. Ion abundances of ions m/z 166 (○), 225 (△) and 239 (□) of pirimicarb at different reagent gas pressures, and at ion source temperatures of 125 (A), 175 (B) and 225°C (C).

NCI in PB-MS was found [37,38]. The upper limit is probably due to the fact that less particles reach the ion source wall; therefore, evaporation of the particles remains incomplete and, consequently, less analyte molecules are available for ionisation. The lower limit is probably determined by the efficiency of the ion formation process, indiscriminate of the type of ions formed. The pressure dependence is not compound-specific, as is evident from our experimental data.

The pressure dependence is less important at higher ion source temperatures, of, typically, 175–225°C. Consequently, the ion intensity data at these temperatures show better repeatability. As expected, an increase of the $[M+H-CH_3NCO]^+$ and $[M+NH_3+H-CH_3NCO]^+$ ion intensities with the ion source temperature is observed for all N-methyl carbamates and although the mechanism of formation of these ions remains unclear, a comparison of DCI and PB–CI spectra makes it likely that they are mainly due to thermal degradation of these compounds. The use of higher ion source temperatures, up to 225°C, is favourable for the total ion current quantitation of some of the carbamates. However, under these conditions, the intensities of the $[M+H]^+$ and $[M+NH_3+H]^+$ ions of all test analytes decrease markedly and selected-ion monitoring is best carried out at low source temperatures, typically 125°C.

4. Conclusions

Mass spectra of selected carbamates were obtained under ammonia PCI conditions and using direct probe or FIA–PB inlet systems. Comparison of spectra from both inlet methods shows that an increase in fragment ion intensities with the ion source temperature under FIA–PB-PCI-MS conditions is due to thermal degradation.

It is observed that both the ion source pressure and the temperature cause irrepeatability of the ammonia PCI mass spectra of carbamates under FIA–PB-MS conditions, with strongest variations for carbofuran. The use of higher ion source temperatures, up to 225°C, is favourable for the total ion current quantitation of some of the carbamates. However, under these conditions, the intensities of the $[M+H]^+$ and $[M+NH_3+H]^+$ ions of all test analytes decrease markedly and selected-ion monitoring is best carried out at low source temperatures, typically 125°C. As a consequence it is of utmost importance to use well defined experimental conditions for the quantitative determination of carbamates with LC–PB-PCI-MS. A study on the quantitative determination of carbamates by LC–PB-MS, using on-line preconcentration, will be published in the near future [26].

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