

Thermospray Mass Spectrometry of Diazonium and Di-, Tri- and Tetra-quaternary Onium Salts

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Various diazonium, multiply charged ammonium and pyridinium salts and one diphosphonium salt have been analysed by thermospray (TSP) mass spectrometry. The intact cation forms the base peak in all spectra. Typically only a few, yet structurally significant, ions are observed. For diazonium salts the level of fragmentation can be controlled by the temperature of the TSP interface while the fragmentation of the quaternary salts is found to be rather insensitive to interface temperatures.

INTRODUCTION

Salts containing multiply charged complex cations such as quaternary salts decompose during volatilization. Therefore, they are not amenable to conventional mass spectrometry employing gas phase ionization techniques for molecular weight determination.

In the past new ionization techniques in which ions are directly formed from a solid or liquid state of the sample were used for the analysis of diquaternary compounds. The results obtained by secondary ion mass spectrometry (SIMS),^{1,2} and fast atom bombardment (FAB)^{3,4} and laser desorption (LD)⁵ mass spectrometry show that intact dications are only rarely observed and with low abundance. In field desorption (FD)⁶⁻⁹ mass spectrometry dications are more frequently observed but often as weak signals only. Molecular weight information can also be derived from $[\text{Cat}^{2+}\text{X}^-]$ ions where X^- is a counter-anion. The formation of these ions has been reported for various salts and different ionization techniques.

Mass spectra exhibiting abundant dication signals have been reported for electrohydrodynamic ionization (EH) mass spectrometry,^{10,11} the so-called ion evaporation technique¹² and, more recently, also for thermospray (TSP) mass spectrometry.^{13,14} In the TSP spectra the dications form exclusively the base peak with a low level of fragmentation. TSP mass spectrometry can be regarded as the most promising technique for molecular weight determination of multiply charged complex cations.

In the TSP mass spectrometry pioneered by Vestal *et al.*^{15,16} for on-line liquid chromatography mass spectrometry coupling, soft ionization of polar molecules is achieved by protonation and/or NH_4^+ attachment. To this end a TSP electrolyte such as

ammonium acetate is added to the mobile phase. However, for desolvation of dications of quaternary salts the use of TSP electrolytes has proved to be disadvantageous, i.e. resulting in enhanced fragmentation and a reduced signal-to-noise ratio.¹⁴ These effects of TSP electrolytes have been attributed to the formation and decomposition of solid particles which play a significant role in the generation of ions by TSP.¹⁴

This paper reports results of a study of liquid chromatography (LC)-independent TSP mass spectrometry of doubly to quadruply charged quaternary salts and of diazonium salts.

EXPERIMENTAL

The laboratory-constructed TSP assembly utilized has been described elsewhere.¹⁷ The pressure of the jet chamber measured in the pump-out line was maintained at 8 mbar. The temperature of the vaporizer, a stainless steel capillary of 80 μm i.d., was between 210 and 270 °C. The jet chamber temperature was varied between 300 and 400 °C for the quaternary salts and between 150 and 250 °C in the case of the diazonium salts.

All the compounds were soluble in water and hence water was used throughout for generating the thermospray jet. No further electrolyte was added. About 0.2 cm^3 aqueous solution of the sample was introduced directly to the TSP interface, i.e. no chromatographic column was utilized. The concentration of the sample was typically about $10^{-3} \text{ mol dm}^{-3}$.

Mass analysis was performed with a Finnigan 400 quadrupole mass filter, having a mass range of 1–420 u. The spectra were obtained by signal accumulation employing a Tracor NS 570 A multichannel analyser.

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Methylviologen, methyl green, tetrazolium blue chloride and all the diazonium salts were purchased from Fluka Chemicals. The quaternary salts were prepared by refluxing solutions of the corresponding free amines or pyridino compounds in DMF for 8 h with excess of methyl iodide and subsequent drying in vacuum. Further details of synthesis of these compounds are described in Refs 18–20.

RESULTS AND DISCUSSION

Quaternary salts

The TSP mass spectrum of a diquaternary salt is shown in Fig. 1. The spectra of further diquaternary ammonium salts (2–7) and of one diphosphonium salt (8) are summarized in Table 1. The intact dication forms the base peak in all spectra. The level of fragmentation is typically low. However, for the compounds 6 and 8 the mass range of the spectrometer did not allow the detection of all fragment ions.

Exclusively singly charged fragment ions are formed. They arise from thermal decomposition of solid particles or desolvated ions in the jet and/or from ion–molecule reactions. $[\text{Cat} - \text{CH}_3]^+$ ions resulting from dealkylation reactions²¹ are most

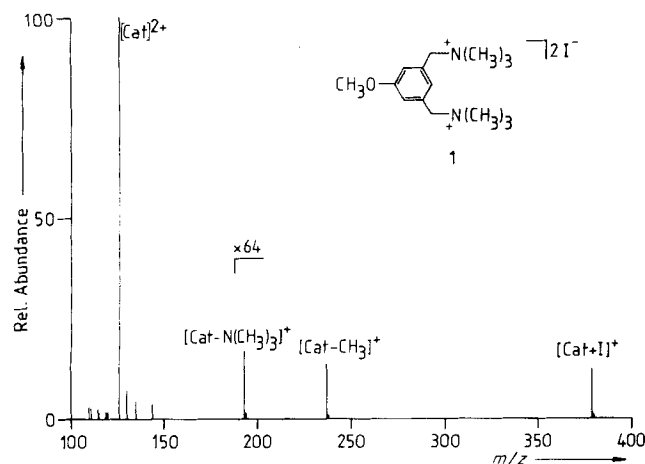
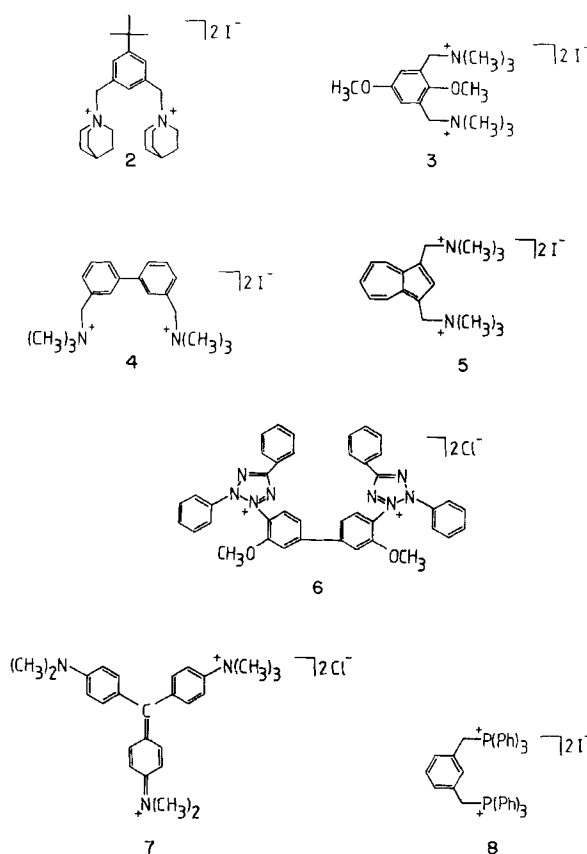


Figure 1. TSP mass spectrum of a diquaternary ammonium salt.

Table 1. TSP mass spectra of some diquaternary salts

Compound (mass of dication)	<i>m/z</i> of ions (% rel. abund.)
2 (382)	112 (80); 125 (5); 191 (100); 272 (15)
3 (282)	141 (100); 150 (5); 163 (3); 208 (1); 267 (5)
4 (298)	130 (20); 141 (20); 149 (100); 240 (1)
5 (272)	130 (50); 136 (100); 145 (5); 155 (10); 171 (15); 230 (5); 247 (10); 257 (5)
6 (656)	328 (100)
7 (387)	193.5 (100); 203 (2); 358 (1); 363 (1); 372 (10); 386 (1); 388 (2); 404 (10)
8 (628)	314 (100); 367 (35)



frequently found in the spectra. Removal of the two charges of the cation by demethylation reactions and subsequent ionization of the neutral fragment by protonation leads to $[\text{Cat} - 2\text{CH}_3 + \text{H}]^+$ ions. The nitrogen heteroatoms have a particularly high proton affinity. Proton donors are provided by H_3O^+ , NH_4^+ and other impurities. A structure assignment is possible for most of the fragment ions of Table 1.

As shown in Fig. 2 a high coulomb repulsion between the two charges of a dication facilitates the formation of fragment ions. For example the $[\text{Cat} - \text{CH}_3]^+$ ion is significantly more abundant in Fig. 2 than in Fig. 1. The peaks around the $[\text{Cat}]^{2+}$ signal in Fig. 2 are due to $[\text{Cat}^{2+}(\text{H}_2\text{O})_n]$ with $n = 1-4$. Further peaks in the lower mass range of this and other TSP spectra shown in this paper result from unidentified impurities and from H_3O^+ , Na^+ , K^+ and NH_4^+ ions with water molecules attached. The $[\text{Cat} - \text{H}]^+$ ion is probably formed via proton abstraction and ring opening from the $[\text{Cat}]^{2+}$, analogous to a Hofmann degradation.^{21,22}

$[\text{Cat} + \text{X}]^+$ ions with $\text{X} = \text{Cl}, \text{I}$ are typically of low abundance which reflects more the thermal instability of this ion with respect to chemical degradation reactions than the coulomb binding energy between the cation and anion. Accordingly, the $[\text{Cat}^{2+}(\text{H}_2\text{O})_n]$ signals in Fig. 2 are more abundant than the $[\text{Cat} + \text{I}]^+$ peak. This is in contrast to expectations derived from the difference in coulomb binding energies between $[\text{Cat}]^{2+}$ and H_2O and $[\text{Cat}]^{2+}$ and I^- respectively.

Spectra similar to those of diammonium salts are obtained for dipyrindinium salts. However, in addition to the $[\text{Cat}]^{2+}$ the singly charged $[\text{Cat}]^{+}$ ion is formed.

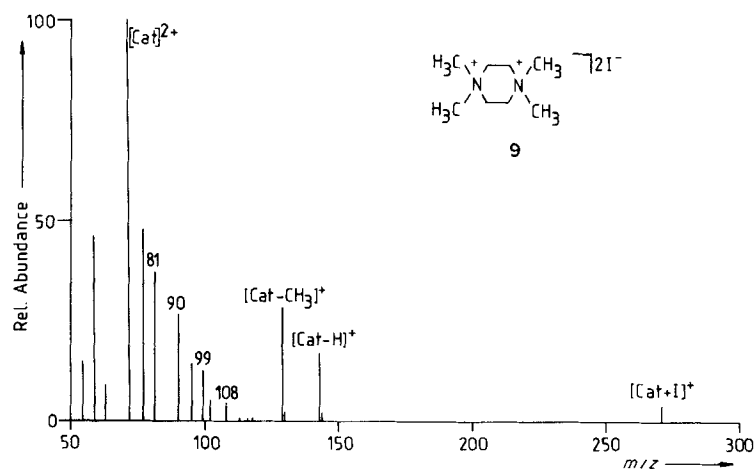


Figure 2. TSP mass spectrum of compound 9.

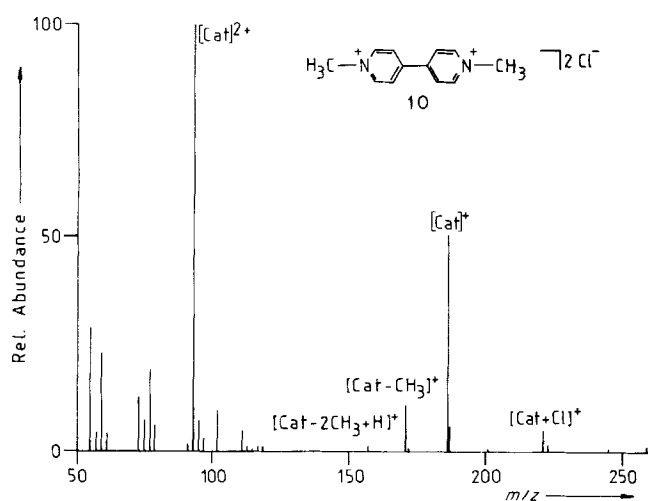


Figure 3. TSP mass spectrum of a diquaternary pyridinium salt.

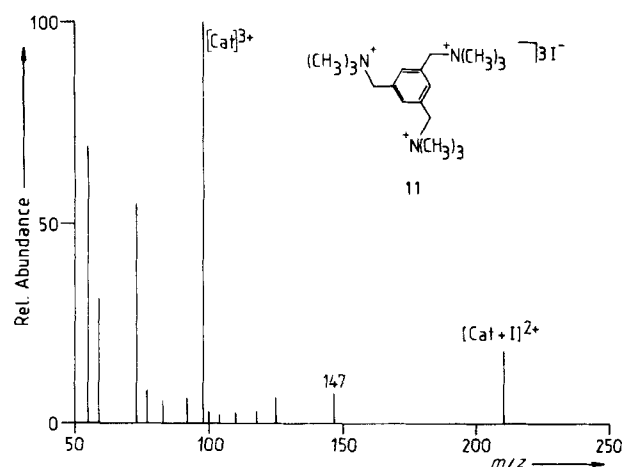


Figure 4. TSP mass spectrum of a triquaternary ammonium salt.

This is illustrated in Fig. 3 for methylviologen. Quaternary pyridinium ions can easily accept electrons leading to rather stable radicals. Accordingly, $[\text{Cat}]^{+}$ ions have been observed in SI and FAB mass spectra of diquaternary pyridinium salts.^{1,3,4}

In general, the relative intensities of fragment ions in TSP spectra of diquaternary pyridinium and ammonium salts are only slightly dependent on the temperature of the capillary and the jet chamber although the total ion current varies strongly with the temperature of vaporization of the aqueous sample solution. This can be attributed to a high thermal stability of the dications in the gas phase, i.e. of dications isolated from counter-ions.

Abundant ion signals even of intact cations of tri- and tetraquaternary salts have been obtained as shown in Figs 4 and 5. Unfortunately the available mass range of the quadrupole covers only a fraction of that required for detection of all fragment ions. The spectra of Figs 4 and 5 also exhibit doubly and triply charged ions, respectively, as indicated. For the tetrapyrindinium ion of Fig. 5 (12) charge reduction by electron attachment is to be expected as discussed

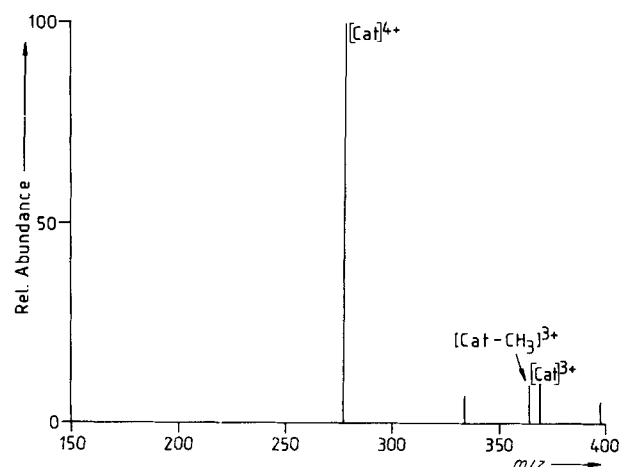
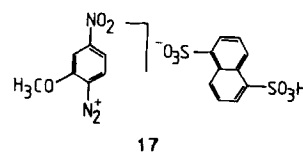
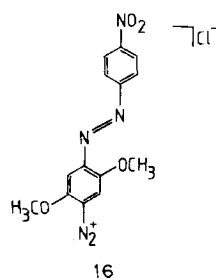
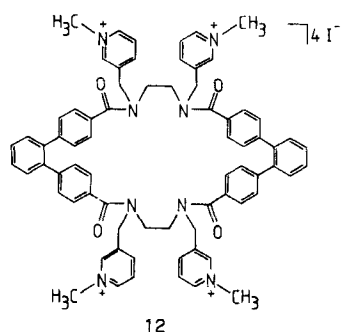


Figure 5. TSP mass spectrum of a tetraquaternary pyridinium salt (12). Molecular weight of the cation: 1108 u.

above. In Fig. 4 the ion signals around the $[\text{Cat}]^{3+}$ arise from impurities and water attachment to the cation. The peak at m/z 147 is probably also an impurity and not a $[\text{Cat}]^{2+}$ signal.



Diazonium salts

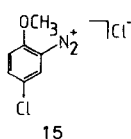
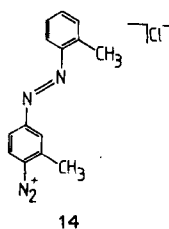
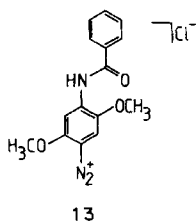
Diazonium salts are thermally very labile due to the ease of eliminating the diazonium group via N_2 formation. Therefore, diazonium salts are difficult to analyse by mass spectrometry even by applying soft ionization techniques such as FAB.²³

Several diazonium salts (13–17) commercially available have been investigated by TSP mass spectrometry. As shown in Table 2 all spectra exhibit the diazonium cation as the base peak. Fragmentation reactions lead to $[Cat - N_2]^+$, $[Cat - N_2 + 2H]^+$ and $[Cat - N_2 + H_2O]^+$ ions. The latter ion is easily explained by solution chemistry.

Table 2. TSP mass spectra of some diazonium salts

Compound (mass of cation)	<i>m/z</i> of ions (% rel. abund.)
13 (284)	258 (5); 274 (5); 284 (100); 302 (1)
14 (237)	209 (5); 211 (5); 227 (60); 237 (100)
15 (169/171)	169/171 (100/30); 187/189 (5/2)
16 (314)	314 (100)
17 (180)	180 (100); 198 (1)

The fragmentation of diazonium cations was found to be sensitively dependent on the temperature of the capillary and the jet chamber. This effect of temperature on the spectra is qualitatively the same as that reported earlier for a dication salt with two diazonium groups.¹⁴ The dication formed again the base peak in the TSP spectrum of this salt.



Comment on the ion formation

The abundant cation signals in the TSP spectra of the reported onium salts indicate an ionization mechanism in which the cations are at first separated from the counter-ions in the liquid phase via droplet formation. The ions are subsequently desolvated from the droplet by thermal evaporation of the solvent. The fraction of ions in the spectra which can be attributed to a decomposition of charged solid particles or salt cluster molecules is very small.¹⁴ We believe that the separation of the cations from anions is not so much the result of a field-induced ion evaporation mechanism²⁴ but rather arises from disintegration processes of small charged droplets caused by Rayleigh instabilities^{25,26} or by a direct thermal generation of extremely fine randomly charged droplets from the mobile phase.

The minor contribution of an ion evaporation mechanism to the desolvation of the cations is supported by the observation of abundant $[Sr^{2+}(H_2O)_n]$ and $[Ba^{2+}(H_2O)_n]$ ion signals with $n = 2-12$ in the TSP spectra of the corresponding metal chlorides without or with only weak additional signals of singly charged ions formed by attachment of Cl^- to the metal ions.²⁷ According to Iribarne and Thomson,^{28,29} these ionization phenomena can hardly be explained by an ion evaporation mechanism. However, a detailed discussion of the ionization mechanism contributing to TSP spectra is beyond the scope of this paper.

CONCLUSION

The capability of TSP mass spectrometry appears to be unique for the analysis of diazonium salts and of onium salts with multiply charged cations. The spectra demonstrate soft ionization conditions and a high thermal stability of the multiply charged ions in the gas phase, if separated from the counter-ion. It has to be emphasized that for the TSP ionization of these salts no electrolyte such as ammonium acetate was added. The addition of a TSP electrolyte results in enhanced fragmentation and decreased signal-to-noise ratio.¹⁴

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REFERENCES

1. T. M. Ryan, R. J. Day and R. G. Cooks, *Anal. Chem.* **52**, 2054 (1980).
2. S. M. Scheifers, S. Verma and R. G. Cooks, *Anal. Chem.* **55**, 2260 (1983).
3. D. F. Barofsky and U. Giessmann, *Int. J. Mass Spectrom. Ion Phys.* **46**, 359 (1983).
4. D. N. Heller, J. Yergey and R. J. Cotter, *Anal. Chem.* **55**, 1310 (1983).
5. T. A. Dang, R. J. Day and D. M. Hercules, *Anal. Chem.* **56**, 866 (1984).
6. G. W. Wood, J. H. McIntosh and P. Y. Lau, *J. Org. Chem.* **40**, 636 (1975).
7. M. C. Sammons, M. M. Bursey and C. K. White, *Anal. Chem.* **47**, 1165 (1975).
8. C. N. McEwen, S. F. Layton and S. K. Taylor, *Anal. Chem.* **49**, 922 (1977).
9. P. Dähling and F. W. Röllgen, unpublished results.
10. K. D. Cook and K. W. S. Chan, *Int. J. Mass Spectrom. Ion Proc.* **54**, 135 (1983).
11. S. L. Murawski and K. D. Cook, *Anal. Chem.* **56**, 1015 (1984).
12. B. A. Thomson, *Proceedings 32nd Annual Conference on Mass Spectrometry and Allied Topics*, p. 190, San Antonio (1984).
13. G. Schmelzeisen-Redeker, U. Giessmann and F. W. Röllgen, *Angew. Chem. Int. Ed.* **23**, 892 (1984).
14. G. Schmelzeisen-Redeker, M. A. McDowall, U. Giessmann, K. Levsen and F. W. Röllgen, *J. Chromatogr.* **323**, 127 (1985).
15. C. R. Blakley, J. J. Carmody and M. L. Vestal, *J. Am. Chem. Soc.* **102**, 5933 (1980).
16. C. R. Blakley and M. L. Vestal, *Anal. Chem.* **55**, 750 (1983).
17. G. Schmelzeisen-Redeker, U. Giessmann and F. W. Röllgen, *J. Phys. (Paris)* **45**, C9-297 (1984).
18. H. G. Löhr, H. P. Josel, A. Engel, F. Vögtle, W. Schuh and H. Puff, *Chem. Ber.* **117**, 1487 (1984).
19. H. G. Löhr, A. Engel, H. P. Josel, F. Vögtle, W. Schuh and H. Puff, *J. Org. Chem.* **49**, 1621 (1984).
20. F. Vögtle, W. M. Müller, U. Werner and J. Franke, *Naturwissenschaften* **72**, 155 (1985).
21. M. Hesse and F. Leutzing, *Adv. Mass Spectrom.* **4**, 163 (1968).
22. H. J. Veith and M. Hesse, *Helv. Chim. Acta* **52**, 2004 (1969).
23. K. P. Wirth, S. S. Wong and F. W. Röllgen, unpublished results.
24. M. L. Vestal, in *Ion Formation from Organic Solids*, ed. by A. Benninghoven, Springer, Heidelberg (1983).
25. Lord Rayleigh, *Phil. Mag.* **14**, 184 (1882).
26. U. Giessmann, Dissertation, Bonn (1981).
27. G. Hambitzer, G. Schmelzeisen-Redeker and F. W. Röllgen, unpublished results.
28. J. V. Iribarne and B. A. Thomson, *J. Chem. Phys.* **64**, 2287 (1976).
29. B. A. Thomson and J. V. Iribarne, *J. Chem. Phys.* **71**, 4451 (1979).

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