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Characterization of Organic Cations of Synthetic Interest by Desorption Ionization and Tandem Mass Spectrometry

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Pyrylium and pyridinium salts give intact cations and structurally diagnostic fragment ions when examined by the desorption methods of ionization, including secondary ion mass spectrometry (SIMS), fast atom bombardment (FAB), and laser desorption (LD). Comparisons are made between these methods and also with the results of electron ionization (EI). The effects on the mass spectra of diluting the sample in both solid and liquid matrices are explored. Control of ion internal energy, and hence of the degree of fragmentation, is possible by preparing samples from ammonium chloride and other salt matrices. A beam-induced pyrylium to pyridinium salt conversion, analogous to the solution reaction, is demonstrated in the presence of ammonium chloride. The same process is shown to occur in the gas phase when ammonia is used as a chemical ionization reagent gas. In the SIMS analysis of amines, this conversion is useful as a reverse derivatization reaction. The mass spectrometry/mass spectrometry (MS/MS) experiment, which establishes ionic relationships, is used to establish the role of unimolecular reactions in creating the fragment ions observed in desorption ionization spectra and is also used to characterize particular ions common to the several ionization methods.

Introduction

Pyrylium salts are important synthetic intermediates[1] in part because of their ready reaction with primary amines to form pyridinium salts which can transfer the N-substituent to nucleophiles.[2] With the development of mass spectrometric methods which allow the direct examination of organic salts,[3-6] it is appropriate to examine representative pyridinium and pyrylium salts by several of these desorption ionization techniques. This study also utilizes the capabilities of tandem mass spectrometry[7-10] for establishing ionic relationships and for ion structure characterization.

The mass spectra of organic salts have traditionally been studied by electron ionization (EI), which often produces ions corresponding to thermal degradation products.[11-14] However, the spectra can still be related to the unperturbed structure. Molecular secondary ion mass spectrometry[15] is a desorption ionization (DI) method[16] well-suited to the sampling of preformed ions directly from the condensed phase. Using this technique, organic salts give spectra which show no evidence of thermal degradation of the type reported in the electron ionization mass spectra.[17,18] Comparable spectra are often obtained by the related methods of laser desorption (LD) and fast atom bombardment (FAB).

Tandem mass spectrometry (MS/MS)[19,20] is useful in the determination of ion structures. As used here, a mass-selected ion, termed the parent ion, is forced to dissociate by an energetic collision with a gas molecule. The resultant fragment ions, termed daughter ions, are then analyzed to form the MS/MS spectrum. The high intrinsic sensitivity of the mass spectrometer and the immunity of the MS/MS experiment to chemical noise allows characterization of even those ions which represent the products of low yield reactions occurring in the ion source.

Specific objectives are as follows: (i) to establish the utility of secondary ion mass spectrometry (SIMS) in providing mass spectra of representative pyrylium and pyridinium salts, (ii) to compare other techniques of ionization, especially laser desorption (LD) and fast atom bombardment (FAB) with SIMS, (iii) to seek a mass spectrometric analogy to the pyrylium → pyridinium salt conversion reaction, and (iv) to employ tandem mass spectrometry to investigate some of the ion chemistry of these salts.

Experimental Section

All positive ion SIMS spectra were obtained with a commercial Riber instrument (Model SQ 156L) which has been described in detail.[21] Samples were burnished onto a roughened 0.005-in.-thick silver foil (1 cm^2 area). A primary beam of 4.5 keV argon ions was used to bombard the sample at an angle of incidence of 45°. The primary beam current density was 1×10^{-9} A/cm^2 or less; the beam was focused on a 10-mm^2 spot. This current allows

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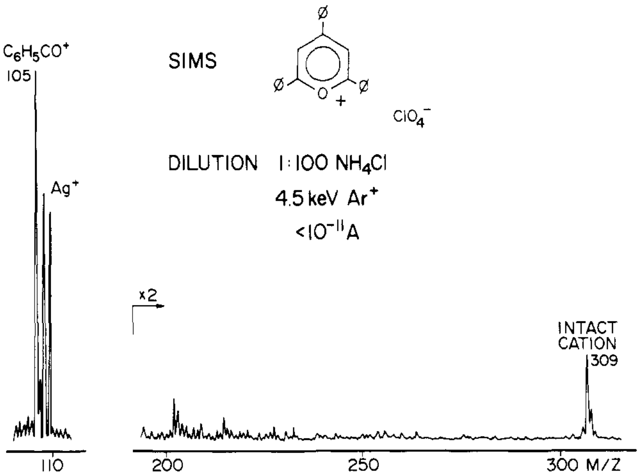


Figure 1. Positive ion SIMS spectrum of 2,4,6-triphenylpyrylium perchlorate contains the intact cation at m/z 309 and the fragment ion at m/z 105. The positive spectrum is independent of the nature of the counterion. Comparisons with MS/MS data show that the fragmentation occurs in the gas phase rather than at the surface.

operation under the conditions of static SIMS,[22] that is, conditions under which no damage to the organic sample is observable in the course of data collection. Increases of the primary ion flux to 1×10^{-7} A/cm^2 were used in experiments which attempted to induce surface reactions. Secondary ions were extracted normal to the surface into a broad pass energy filter set to transmit molecular ions of low translational energy and then passed into a quadrupole mass analyzer coupled to a pulse counting detection system. Relative abundances of ions in the positive ion SIMS spectra are observed with a sample-to-sample reproducibility of 10–15%.

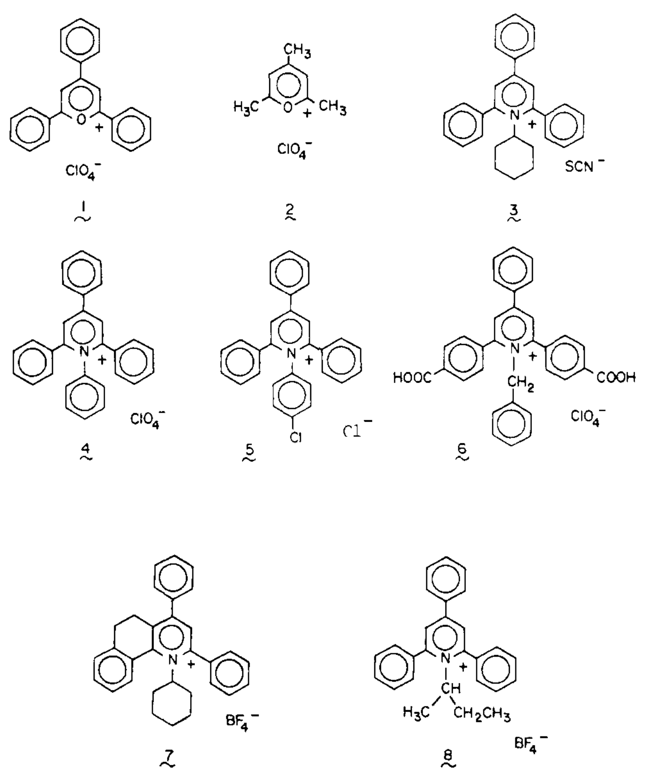
Electron-ionization mass spectra and MS/MS spectra were obtained at low collision energy (20 eV) on a Finnigan TSQ triple quadrupole mass spectrometer equipped with a INCOS data system.[23] Mass spectra were recorded by scanning the third quadrupole. MS/MS data were obtained by utilizing the second quadrupole in the rf-only mode as a combined focusing device and collision cell. Argon was used as the neutral target gas. Collisionally activated decomposition of the mass-selected parent ion produces a daughter ion MS/MS spectrum, recorded by scanning the third quadrupole. Solid samples were introduced into the mass spectrometer via the direct insertion probe heated to a temperature of 300 °C.

The laser desorption experiments were performed with a continuous wave CO_2 laser (Laackman Model RF 88) and the triple quadrupole instrument. Laser power is estimated at 8 W, produced at a wavelength of 10.6 μm. Samples burnished onto a silver substrate were irradiated by the laser beam (1-mm diameter spot size and 45° angle of incidence) which entered the source through a sodium chloride window fitted to an auxiliary port. The filament was not on during these experiments. MS and MS/MS data were recorded as described above for electron ionization.

Fast atom bombardment spectra were recorded (courtesy of Dr. S. E. Unger) using an Iontech gun attached to a ZAB 1F mass spectrometer. The neutral flux is estimated as 10^{-6} A/cm^2. The sample was dissolved in sulfolane or was admixed with ammonium chloride for these experiments; the angle of incidence is 70°.

Samples were synthesized as described previously: 2,4,6-triphenylpyrylium perchlorate (**1**; lit.[24] mp 290 °C); 2,4,6-triphenylpyrylium tetrafluoroborate (lit.[25] mp 253–255 °C); 2,4,6-trimethylpyrylium perchlorate (**2**; lit.[26] mp 244 °C); 1-cyclohexyl-2,4,6-triphenylpyridinium thiocyanate (**3**; lit.[27] mp 151–153 °C); 1,2,4,6-tetraphenylpyridinium perchlorate (**4**; lit.[28] mp 263 °C); 1-(4-chlorophenyl)-2,4,6-triphenylpyridinium chloride (**5**; lit.[29] mp 320–324 °C); 1-benzyl-2,6-di(4-carboxyphenyl)-4-phenylpyridinium perchlorate (**6**; lit.[30] mp >330 °C); 1-cyclohexyl-5,6-dihydro-2,4-diphenylbenzo[*h*]quinolinium tetrafluoroborate (**7**; lit.[27] mp 136–139 °C); 1-*sec*-butyl-2,4,6-triphenylpyridinium tetrafluoroborate (**8**; lit.[27] mp 165–167 °C) (see Chart I).

Chart I



Results and Discussion

Secondary Ion Mass Spectra. Figure 1 exhibits the positive ion SIMS spectrum of compound **1**, 2,4,6-triphenylpyrylium perchlorate. The intact cation at m/z 309 is observed (10% relative abundance (RA)). The predominant fragment ion, and the base peak in the spectrum, occurs at m/z 105, assigned as $C_6H_5CO^+$. These are the only species in the spectrum except for Ag^+ ions derived from exposed support. This typifies the SIMS spectra of pyrylium and pyridinium salts, which usually consist of the intact cation and a few structurally informative fragment ions. The nature of the counterion seems to have no effect on the spectrum obtained. In keeping with this example, the spectrum of the trimethyl-substituted pyrylium salt (**2**) is also simple, exhibiting as the base peak the intact cation at m/z 123 and the fragment ion 105^+ in lesser abundance (5% RA).

The SIMS spectra of a series of substituted pyridinium salts (compounds **3**–**8**) were also investigated. These will be referred to as derivatives of the 2,4,6-triphenylpyridinium salt, with the substituent group bound to the quaternary nitrogen. The SIMS spectrum of the cyclohexyl derivative (**3**) contains the intact cation at m/z 390 (15% RA), as shown in Figure 2b. As is usual in SIMS

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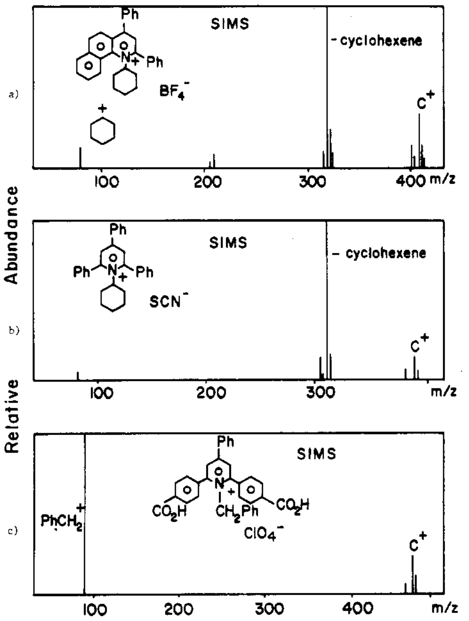

Figure 2. Positive ion SIMS spectra of these pyridinium salts contain intact cations and but a few fragment ions. Losses of neutral molecules from the cation are often observed.

spectra of preformed organic ions, the dominant fragment ions result from the losses of simple neutral molecules. Loss of cyclohexene occurs from the intact cation of **3** to yield an ion at *m/z* 308 which corresponds to the unsubstituted pyridinium cation. Similar thermal decomposition of *N*-alkylpyridinium cations to yield olefins is known.[31] Further loss of benzene (again a neutral molecule) produces a low abundance fragment ion at *m/z* 232 (7% RA) and loss of cyclohexadiene at *m/z* 230 (7% RA). The only other fragment ion in significant abundance observed in the SIMS spectrum of **3** corresponds to the cyclohexyl cation, *m/z* 83.

None of the above behavior is exceptional; it follows patterns established recently for the SIMS spectra of phosphonium[17] and other ammonium salts.[32,33] The spectra are generally useful in that they contain both information on molecular weights and ion structure via diagnostic fragment ions. An exception is the SIMS spectrum of the phenyl-substituted pyridinium salt **4**. The intact cation at *m/z* 384 is observed as the base peak with both good signal/noise ratio and an extended signal persistence.[34] However, *no* fragment ions are observed. This resistance to fragmentation persists even when the flux of the primary ion beam is increased several orders of magnitude and the period of exposure is extended to several hours. The neutral molecule expected to be lost from this structure is benzyne, and it is lost in the SIMS spectra of related phosphonium salts.[17] The high enthalpy of this fragment apparently prevents this process in the present example. Other possible reactions are formation of the phenyl cation, generation of which must involve the cleavage of the strong phenyl–nitrogen bond and elimination of benzene. This last process would leave the positive charge on the heteroatom, but it may be unfavorable because of the sole availability of aromatic hydrogen atoms.

The 4-chlorophenyl derivative, **5**, gives a SIMS spectrum similar to that of **4**. The cation at *m/z* 418 produces a persistent base peak of good signal/noise ratio with the expected chlorine isotopic peak at *m/z* 420 in the ratio of approximately 3:1. Again, no fragment ions are observed even when the primary ion flux is increased by two orders of magnitude. In these two cases, the SIMS spectra are useful for cationic weight determination and ideal for quantitation. This stability of *N*-arylpyridinium cations is paralleled by their solution chemistry, which is characterized by the resistance of the N-aryl bond to cleavage.[35] On the basis of these arguments and of solution chemistry precedents,[36] one would predict that the benzyl derivative, **6**, would readily undergo N–C heterolysis; the base peak in the spectrum does indeed occur at *m/z* 91, nominally $C_7H_7^+$ the tropylium ion. The intact cation at *m/z* 486 (22% RA) was virtually the sole other peak in the spectrum (Figure 2c). Finally, the SIMS spectrum of the pyridinium salt **7** (Figure 2a) contains the intact cation at *m/z* 416 15% RA), which fragments by loss of cyclohexene (as did the related compound **3**) to produce here a fragment ion at *m/z* 334 (base peak). loss of cyclohexane gives the fragment at *m/z* 332 (9% RA); alternatively, this process can be viewed as dehydrogenation of the ion at *m/z* 334. The possibility that this is a cyclization product cannot be ruled out. Other pyridinium salts whose spectra are not displayed typically show a small abundance (5–10% RA) of ions at masses corresponding to dehydrogenation products.

Fast Atom Bombardment Spectra. In fast atom bombardment (FAB), a high energy ion beam is neutralized by charge exchange before it impacts a surface. The experiment is often done (i) using higher primary beam fluxes than in static SIMS and (ii) with solutions of the analyte in vacuum compatible solvents. To compare SIMS and FAB spectra under similar conditions of sample preparation, trimethylpyrylium tetrafluoroborate was mixed (1:3) with solid ammonium chloride,[34] and its FAB spectrum recorded. Two ions were observed corresponding to the intact cation at *m/z* 123 and the fragment formed by loss of water at *m/z* 105. This spectrum is analogous to that observed in SIMS. The main difference in the two experiments concerns the intensity of ions produced and the duration of the secondary ion signal. The ion yield in FAB appears to be several orders of magnitude greater than that observed under static SIMS conditions, corresponding to the larger primary particle flux. The secondary ion current of the solid sample lasted for minutes at high fluxes as opposed to hours under the reduced level of irradiation. A more subtle but significant difference was the absence of an ion at *m/z* 308 corresponding to the formation of the pyridinium ion from the pyrylium salt (vide infra).

The FAB spectrum of the *sec*-butyl derivative **8** was recorded first from a solid mixture with excess ammonium chloride and second, in the more conventional way, from a solution in sulfolane in order to compare the spectra obtained. The spectrum recorded from the ammonium chloride matrix is given in Figure 3; the ion signal is very intense, but of short duration. It is rapidly (ca. 30 s) replaced by a spectrum rich in ammonium chloride cluster ions.[37] Scratching of the surface (used in early molecular SIMS work to increase ion emission and persistence)

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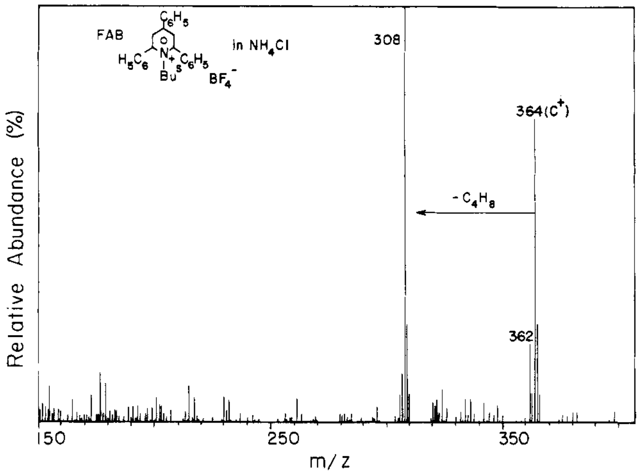

Figure 3. Positive ion FAB spectrum of *sec*-butyl-2,4,6-triphenylpyridinium tetrafluoroborate in a matrix of ammonium chloride contains the intact cation at *m/z* 364 and the fragment ion of butene loss, *m/z* 308.

recreated the spectrum of the analyte in its original intensity, and it again rapidly faded to be replaced by NH_4Cl cluter ion emission.

The FAB spectra of compound 8 obtained from both matrices are similar. The intact cation, *m/z* 364, fragments by butene loss to give the base peak, *m/z* 308. The butyl ion ($C_4H_9^+$, *m/z* 57) corresponding to the product of solvolysis, does not appear with significant abundance in either spectrum. Points of difference between the two FAB spectra include (i) the presence of a $(C-2)^+$ ion from dehydrogenation in the spectrum taken from the solid (this process is thought to be a surface reaction rather than a normal gas phase fragmentation), (ii) the presence of solvated cations desorbed from the solution matrix (these clusters contain one or two molecules of sulfolane associated with the pyridinium cation), and (iii) observation of the ion-pair form of cluster ion, in this case consisting of two cations and an anion, in the spectrum taken from the sulfolane matrix.

MS/MS Analysis of Ions from Pyrylium and Pyridinium Salts. Djerassi et al.[11] discovered in an electron ionization (EI) study of pyrylium halides that the principal fragmentation process was elimination of hydrogen halide, except for the various halide salts of 2,4,6-triphenylpyrylium cation, the spectra of which contained ions at the mass of the intact cation. The present study confirms this latter result. In the EI mass spectrum off 2,4,6-triphenylpyrylium tetrafluoroborate, the ion at *m/z* 309 (which would correspond to the intact cation) is observed in high relative abundance; fragment ions at *m/z* 231, 203, 202, 105, and 77 and the doubly-charged ion 309^{2+} are observed. As discussed, the SIMS spectrum contains an ion corresponding to the intact cation at *m/z* 309, but the only fragments observed are those of *m/z* 105 and 77. Neither loss of benzene to form 231^+, loss of benzaldehyde to form 203^+, nor formation of the doubly-charged parent ion is noted in the SIMS spectrum (Figure 1). In order to establish whether fragmentation of 309^+ is a gas phase or a surface phenomenon, the MS/MS spectrum of 309^+ formed in an EI source was obtained and is shown in Figure 4a. This parent 309^+ ion dissociates on collision by losses of benzene (to give 231^+), benzaldehyde (to give 203^+), and facile fragmentation to *m/z* 105 and 77 (most abundant peaks). Thus, the fragmentation observed in the SIMS spectrum is consistent with that which occurs unimolecularly. The more extensive fragmentation in the EI spectrum indicates that SIMS is a "softer" ionization technique. The cation is lifted from the condensed phase without excessive energization and subsequently fragments in the gas phase.

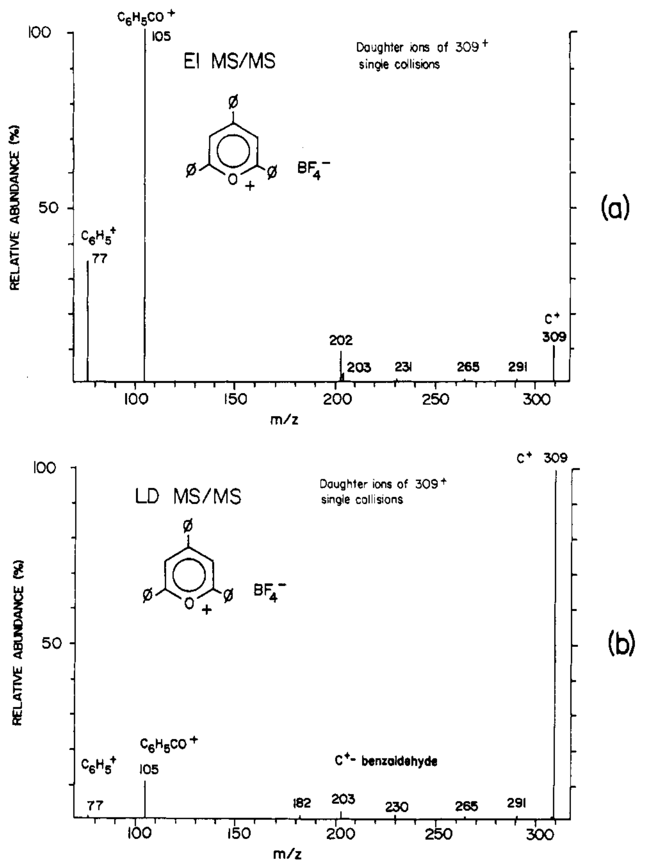

Figure 4. (a) EI MS/MS spectrum of 2,4,6-triphenylpyrylium tetrafluoroborate. The parent 309^+ ion dissociates upon collision by losses of benzene (*m/z* 231) and benzaldehyde (*m/z* 203), and fragmentation to *m/z* 105 and 77 (most abundant peaks). (b) LD MS/MS spectrum of 2,4,6-triphenylpyrylium tetrafluoroborate shows the intact cation at *m/z* 309 and predominant fragment ion at *m/z* 105. Fragmentation from the parent is less than when it is formed by electron ionization.

The MS/MS spectra of the ion at *m/z* 309^+ from 2,4,6-triphenylpyrylium tetrafluoroborate formed in a variety of ionization methods has been investigated in detail.[38] Laser desorption mass spectrometry was used to generate 309^+ from this compound, and the MS/MS spectrum is given in Figure 4b. The ion at *m/z* 309 fragments to give 105^+ as the predominant product; smaller abundances of ions at *m/z* 77 and 203 are noted. These are the same fragment ions noted in the MS/MS spectrum of 309^+ generated by EI (Figure 4a), but the abundances of the fragment ions relative to the parent ion are reduced in the LD MS/MS spectrum. These data either suggest a different structure for the 309^+ generated in these two ionization methods or perhaps an internal energy effect on the MS/MS spectra obtained.

Transformation of Pyrylium to Pyridinium Salt. In solution, substituted pyrylium salts react with a variety of amines to form activated pyridinium salts,[1,2] these transformations generally proceed in high yield. In reverse derivatization reactions which have been developed for desorption ionization mass spectrometry,[39] a reagent is used to transform neutral molecules of analyte into charged

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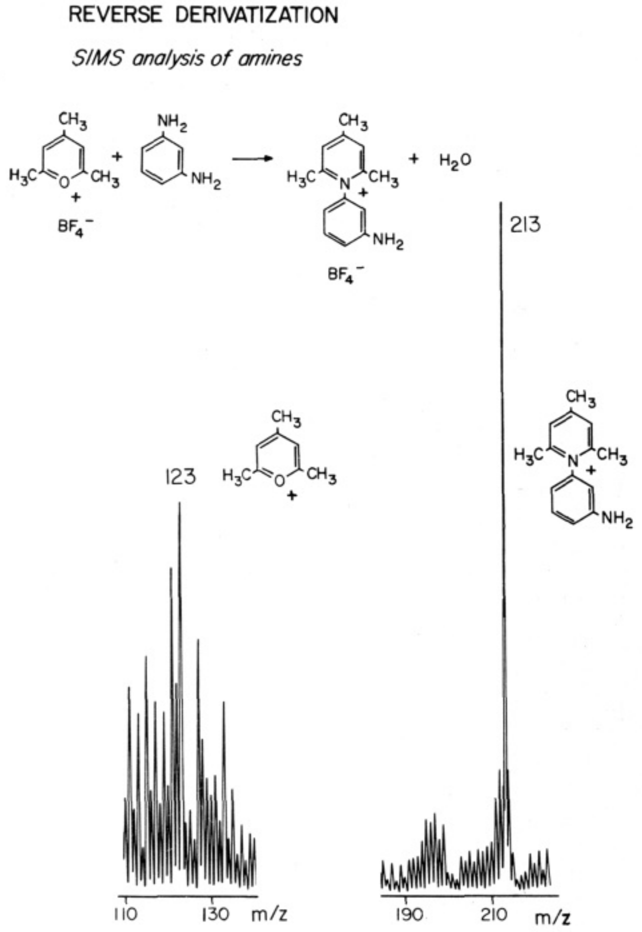


Figure 5. Use of 2,4,6-trimethylpyrylium tetrafluoroborate as a reverse derivatization reagent allows the characterization of the neutral compound *m*-phenylenediamine as a charged species at a mass (*m*/*z* 213) at which interference from background is reduced.

species which are preferentially sampled. Use of pyrylium salts as derivatization reagents provides a means by which amines can be transformed into and analyzed as the corresponding pyridinium salts. Figure 5 shows the result obtained when *m*-phenylenediamine is physically mixed with a small amount of 2,4,6-trimethylpyrylium tetrafluorobrate and burnished as the solid onto a silver planchette. The reaction yields the pyridinium salt with a cation at *m*/*z* 213, which is observed in the SIMS spectrum with much greater abundance than the ion (*m*/*z* 123) due to the reagent pyrylium cation. The cations of the products are increased in mass and interference is reduced. By varying the substituents of the pyrylium salt, the mass at which the analyte is observed can be appropriately selected.

The transformation of pyrylium to pyridinium salts occurs in gas phase reactions as well. Ammonia is often used as a chemical ionization reagent gas, transferring a proton to a neutral molecule to form $(M + H)^+$. However, 2,4,6-triphenylpyrylium tetrafluoroborate (heated from a direct probe into a standard CI source) reacts with neutral ammonia to form the corresponding pyridinium cation (Scheme I), as shown by observation of a very abundant ion at *m*/*z* 308. To confirm this conclusion, the MS/MS spectrum of *m*/*z* 308 was obtained and found to be identical with the MS/MS spectrum obtained from 2,4,6-triphenylpyridine when introduced into the chemical ionization source and protonated by either ammonia or isobutane. This comparison is shown in Figure 6. The lack of dependence upon the nature of the ionizing reagent gas

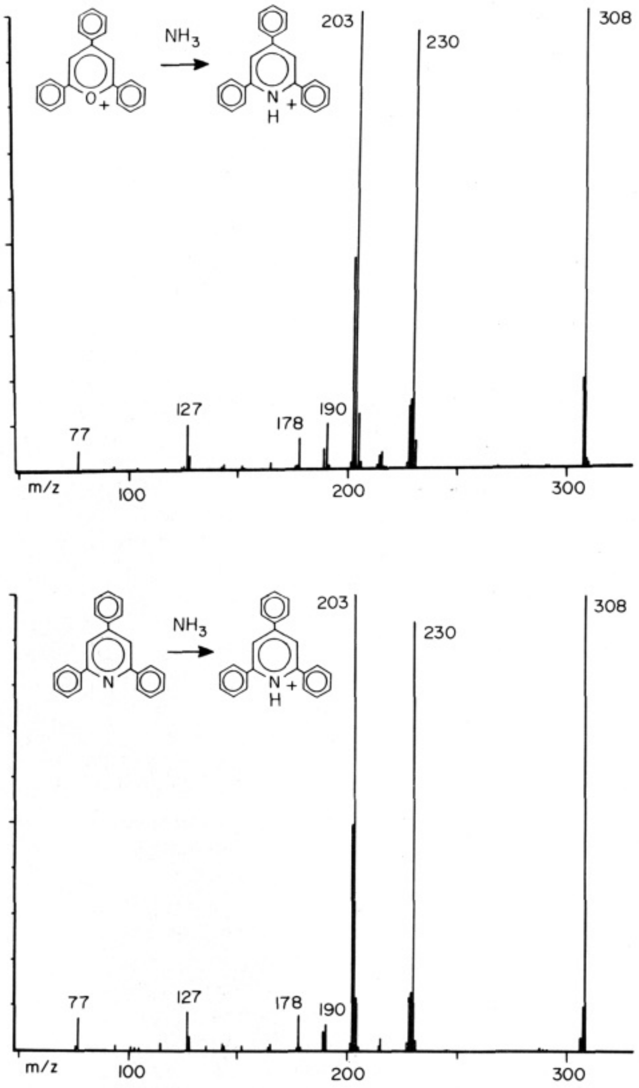
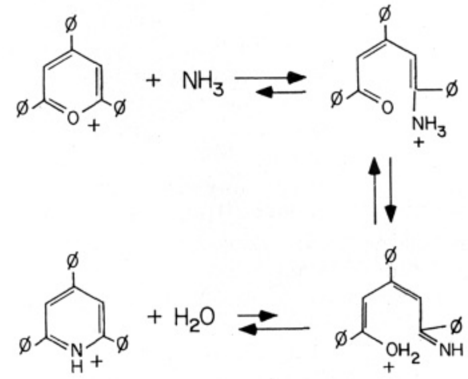


Figure 6. Transformation in the gas phase of the pyrylium cation to the pyridinium cation by reaction with ammonia is confirmed by the identity of the MS/MS daughter ion spectra obtained for the product and the protonated form of the corresponding pyridine.

Scheme I



indicates that the pyridinium ion is formed in both experiments. The transformation process may involve intermediates such as shown in Scheme I, and these have been implicated in the well-understood[40,41] conversion of

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Table I. Effect of Various Methyl Ammonium Salt Matrices on the $105^+/309^+$ Ratio in the SIMS Spectrum of 2,4,6-Triphenylpyrylium Chloride[a]

matrices	$105^+/309^+$ ratio
NH_4Cl	8
$(CH_3)NH_3Cl$	35
$(CH_3)_2NH_2Cl$	24
$(CH_3)_3NHCl$	15
$(CH_3)_4NCl$	7

[a] Constant dilution of 1:100 w:w.

pyrylium to pyridinium in solution. The ammonia CI spectrum of the pyrylium salt does contain an ion at the mass corresponding to the adduct; it dissociates upon collisional activation to yield both *m/z* 309 and *m/z* 308. These ions correspond to the pyrylium (reactant) and the pyridinium (product) cations; the data are therefore consistent with an intermediate(s) which can either dehydrate or deaminate (dehydration is preferred) (Scheme I). Of higher abundance in the ammonia CI spectrum, however, is an ion at *m/z* 325, which corresponds to loss of hydrogen from the intermediate adduct ion at 326^+. This odd electron species, when activated by collision, dissociates primarily by loss of benzene to give the daughter ion at *m/z* 247, and it also forms ions at *m/z* 105 ($C_6H_5CO^+$) and 191 ($C_{15}H_{11}{}^+$).

Matrix Effects. Previous papers have described the effects of an ammonium chloride matrix in SIMS.[34,42] In general, increasing dilution of the sample leads to a decrease in the amount of fragmentation observed, and secondary ion yields can be increased. Similar effects on fragmentation are noted in the SIMS spectra of the compounds of the present study. For instance, SIMS spectra of compound **3** were obtained using the neat compound, and at dilution of the sample in ammonium chloride of 1:2 and 1:20 (w:w). The ratio of the fragment ion 308^+ (loss of cyclohexene) to the intact cation 390^+ varied with the degree of dilution. The initial ratio $308^+/390^+$ of 5/1 in the spectrum of the neat compound changed to a value of 5/4 at a 1:20 matrix dilution but did not change significantly past that point even at dilutions of up to 1:100 000. Similarly, for **6**, a fragment ion/intact cation ratio ($91^+/486^+$) changed from 20/1 in the spectrum of the neat compound to 3.5/1 in the spectrum of the sample diluted 1:2 in ammonium chloride. Significant increases in the relative abundance of the intact cation are obtained with matrix dilution of the sample. In the same experiments, it was noted that despite dilution in ammonium chloride, both absolute ion intensities and sample persistence for these compounds were also increased.

The use of the various methylammonium salts $[(CH_3)_nH_{4-n}N^+Cl^-]$ as matrices in constant dilutions of 1:100 (w:w) was investigated using 2,4,6-triphenylpyrylium tetrafluoroborate as the model compound. The purpose of this study was 2-fold: first, to observe changes in the fragmentation pattern with changes in the matrix, and second, to establish whether bombardment of the alkyl ammonium salt liberates free amine which would then react with the pyrylium salt to form the pyridinium salt (Scheme I). Interaction between the pyrylium salt and beam-generated free amine would be indicated by ions at mass 308 ($n = 0$), 322 ($n = 1$), or 336 ($n = 2$). Ions of low abundance (<5%) corresponding to this reaction were observed in the SIMS spectra when ammonium chloride and methylammonium chloride are used for dilution, but not for any of the other matrices.

An effect of the matrix on the fragmentation pattern was also observed. The ratio of the ion abundances $105^+/309^+$ is shown in Table I as a function of the number of methyl groups in the alkyl ammonium salt used as a matrix. A maximum value of this ratio is observed with methylammonium chloride, and a minimum with ammonium chloride and tetramethylammonium chloride matrices. If, as suggested,[42] the matrix acts to decrease the internal energy of a sputtered cation by a process of desolvation, then it would appear that the symmetrical salts are most effective, and the asymmetrical methylammonium chloride is the least effective.

Conclusions

The SIMS spectra of pyrylium and pyridinium salts provide not only abundant intact cations, but most also contain fragment ions consistent with their structures. The use of MS/MS confirms that fragment ions observed in the spectra are those expected from gas phase decompositions. Ammonium and alkylammonium chloride salt matrices moderate the energy of the sputtered cation, and can reduce the amount of fragmentation observed. Transformation of pyrylium salts to pyridinium salts by reaction with amines can be used in reverse derivatization reactions to characterize neutral amines. Analysis of mixtures of the pyrylium salt with various alkylammonium salt matrices provides evidence of formation of pyridinium salts. MS/MS studies show that the transformation of a pyrylium cation to a pyridinium cation occurs in the gas phase with ammonia; the postulated intermediate can be observed and directly characterized.

The desorption ionization methods of SIMS, FAB, and LD provide similarly useful spectra for this compound class. The spectra are not identical because of the disparate conditions of sample preparation. MS/MS is used to characterize the ion structures of ions formed, and to delineate matrix effects, which are invariably complex. Use of an ammonium chloride matrix extends sample lifetime from a few seconds using the high flux typical of FAB to hours under the low flux conditions used in molecular SIMS.

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Registry No. **1**, 1484-88-4; **2**, 940-93-2; **3**, 88064-53-3; **4**, 25506-69-8; **5**, 71487-79-1; **6**, 88130-97-6; **7**, 88064-66-8; **8**, 75505-87-2; NH_3, 7664-41-7; $(CH_3)NH_3Cl$, 593-51-1; $(CH_3)_2NH_2Cl$, 506-59-2; $(CH_3)_3NHCl$, 593-81-7; $(CH_3)_4NCl$, 75-57-0; NH_4Cl, 12125-02-9; H_2O, 7732-18-5; 2,4,6-triphenylpyrylium perchlorate, 448-61-3; 2,4,6-triphenylpyridinium chloride, 40836-01-9; sulfolane, 126-33-0; 2,4,6-pyrylium, 15959-35-0; 2,4,6-pyridine conjugate acid, 53531-60-5.

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