

Ion/molecule reactions performed in a miniature cylindrical ion trap mass spectrometer

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A recently constructed miniature mass spectrometer, based on a cylindrical ion trap (CIT) mass analyzer, is used to perform ion/molecule reactions in order to improve selectivity for *in situ* analysis of explosives and chemical warfare agent simulants. Six different reactions are explored, including several of the Eberlin reaction type (M. N. Eberlin and R. G. Cooks, *Org. Mass Spectrom.*, 1993, **28**, 679–687) as well as novel gas-phase Meerwein reactions. The reactions include (1) Eberlin transacetalization of the benzoyl, 2,2-dimethyloximinium, and 2,2-dimethylthioximinium cations with 2,2-dimethyl-1,3-dioxolane to form 2-phenyl-1,3-dioxolanylium cations, 2,2-dimethylamine-1,3-dioxolanylium cations and the 2,2-dimethylamin-1,3-oxathiolanylium cations, respectively; (2) Eberlin reaction of the phosphonium ion $\text{CH}_3\text{P}(\text{O})\text{OCH}_3^+$, formed from the chemical warfare agent simulant dimethyl methylphosphonate (DMMP), with 1,4-dioxane to yield the 1,3,2-dioxaphospholanium ion, a new characteristic reaction for phosphate ester detection; (3) the novel Meerwein reaction of the ion $\text{CH}_3\text{P}(\text{O})\text{OCH}_3^+$ with propylene sulfide forming 1,3,2-oxathionylphospholanium ion; (4) the Meerwein reaction of the benzoyl cation with propylene oxide and propylene sulfide to form 4-methyl-2-phenyl-1,3-dioxolane and its thio analog, respectively; (5) ketalization of the benzoyl cation with ethylene glycol to form the 2-phenyl-1,3-dioxolanylium cation; (6) addition/ NO_2 elimination involving benzonitrile radical cation in reaction with nitrobenzene to form an arylated nitrile, a diagnostic reaction for explosives detection and (7) simple methanol addition to the C_7H_7^+ ion, formed by NO_2 loss from the molecular ion of *p*-nitrotoluene to form an intact adduct. Evidence is provided that these reactions occur to give the products described and their potential analytical utility is discussed.

Introduction

Two major thrusts in analytical instrumentation are towards miniaturization of laboratory scale instrumentation and construction of fieldable systems.^{1,2} Fieldable systems are highly desirable for *in situ* analysis of trace level constituents in air or water matrices.^{3,4} Because the compounds of interest often occur at low levels in complex mixtures, their detection can represent a great challenge and require a highly selective and sensitive analytical method.

Although mass spectrometry is the most sensitive and selective general purpose method of chemical analysis, it is often necessary to take extraordinary steps to maximize selectivity. Collision-induced dissociation (CID) of a mass-selected ion and the use of tandem mass spectrometry to characterize its products, increases selectivity over that available in single-stage mass spectrometry.⁵ Ion/molecule reactions offer a method of increasing selectivity that is complementary to CID. In spite of this, ion/molecule reactions have not been widely used in chemical analysis.⁶ The MS^n capability and high pressure tolerance of the Paul ion trap allows ion/molecule reactions and CID to be performed sequentially in order to maximize selectivity for particular compounds.⁷

The purpose of this study is to explore the capability of a recently constructed miniature mass spectrometer,^{8,9} based on a cylindrical ion trap mass analyzer, for trace compound detection using ion/molecule reactions. These demonstration experiments focus on reactions of nitroaromatics and phosphonates, classes of compounds of importance as explosives and chemical

warfare (CW) agent simulants. The reactions studied include simple Lewis acid/base addition, the Eberlin transacetalization, gas phase ketalization, novel gas-phase Meerwein reactions, simple addition, and a nitrile-addition/nitro-elimination reaction.

The Eberlin reaction¹⁰ is a highly-efficient gas-phase reaction involving a cation with amphiphilic character (most typically an acylium ion $\text{R}-\text{C}^+=\text{O}$) and a cyclic acetal or ketal (such as a substituted 1,3-dioxolane). The reaction bears similarities to solution-phase transacetalization. The gas phase ketalization^{11,12} reaction involves the addition of an acylium ion to a neutral diol forming a cyclic ketal. This reaction is analogous to solution phase ketalization¹³ (and the related acetalization), a classical reaction of widespread use which occurs when carbonyl compounds condense with alcohols and diols, and with their sulfur and nitrogen analogs. Similarly, the gas phase Meerwein¹⁴ reaction involves a three- to five-membered ring expansion of epoxides and thio epoxides after addition to acylium ions. This reaction is analogous to the well established solution phase Meerwein¹⁴ reaction, in which a three- to five-membered ring expansion occurs with epoxides and esters (in place of the acylium ions in the gas phase) in the presence of BF_3 to form 1,3-dioxolanylium ion salts.

Recently, the general class of Eberlin reactions has been expanded to include reactions of phosphonium ions ($\text{CH}_3\text{P}(\text{O})\text{OCH}_3^+$) with dioxane to form characteristic cyclic products (1,3,2-dioxaphospholanium ions).¹⁵ In addition, an Eberlin reaction is observed between the phosphonium ion $\text{CH}_3\text{P}(\text{O})\text{OCH}_3^+$ formed from the chemical warfare agent

simulant dimethyl methylphosphonate (DMMP) and 1,4-dioxane.¹⁵ This result has implications for improved selectivity of detection of CW agents in air, since it has been shown that a variety of other classes of multiply-bonded compounds, including ketones, esters and amides, do *not* react in this manner.

Although nitroaromatic compounds are quite unreactive in the condensed phase, the molecular radical cations have formally separate, and highly reactive, charge and radical sites, which may be expected to result in characteristic ion/molecule reactions and thus to allow facile detection of nitroaromatic compounds, including explosives. However, this expectation has not been met until now; among the very few characteristic ion/reactions is that of substituted nitrobenzenes with substituted benzonitrile radical cations in an addition/NO₂ elimination process to form an arylated nitrile cation, Ar⁺N≡CAr' (where Ar, Ar' = aryl).¹⁶ This addition/NO₂ elimination reaction has previously been applied to trinitrotoluene (TNT), as a possible diagnostic reaction for the presence of nitroaromatic explosives.

Experimental

Instrumentation

These experiments were performed using a second-generation miniature mass spectrometer (version 7.0) based on a miniature cylindrical ion trap mass analyzer (internal radius, $r_o = 2.5$ mm) fitted with a membrane introduction sampling system.^{8,9} This instrument (136 W, 28 × 70 × 18 cm, 17 kg, including battery pack), is much smaller than a previous generation prototype miniature mass spectrometer (version 5.0, 200–300 W, 40 × 60 × 50 cm, 55 kg, including battery pack), described elsewhere,^{17,18} although it retains all the capabilities of the previous instrument. As used for these experiments, it is fitted with an electron ionization source, has an upper mass/charge limit of ~450 Th (Thomson = Dalton charge⁻¹)¹⁹, and uses the mass selective instability scan with resonant ejection at $q_z = 0.808$, $\beta_z = 0.7$, $f_{\text{eject}} = 700$ kHz. Detection is by means of an off-axis channeltron electron multiplier and conversion dynode.

MS and MSⁿ Experiments. For MS experiments, the scan function employed had four periods: a 5 ms delay period, a 50 ms ionization time (electrons gated into trap in order to ionize neutral vapors), a 15–30 ms ion cooling period, and a 15 ms analysis period.⁷ In the MSⁿ experiments, the first two periods were immediately followed by an isolation period of 4 ms. During this period, isolation of the ions of interest was performed using the stored waveform inverse Fourier transform (SWIFT) method.²⁰ SWIFT waveforms were calculated using the ion trap simulation program ITSIM, Version 5.0.²¹ Isolation conditions were optimized during each experiment to yield maximum signals for the ions of interest (4 ms SWIFT pulse, center frequency ranging from 250 to 540 kHz, with a 30–130 kHz bandwidth, amplitude 0.04 to 0.05 V). This was followed by a period of 265–1000 ms for ion/molecule reactions of the isolated ions with neutrals in the ion trap. Product ions resulting from the reaction were subjected to a second sequence of steps involving isolation by a SWIFT waveform (4 ms SWIFT pulse, center frequency ranging from 150 to 315 kHz, with a 40–70 kHz bandwidth, amplitude 0.05 to 0.08 V) followed by collisional activation achieved by applying a sine wave with a frequency chosen to match the secular frequency(ies) of the ion(s) of interest. The amplitude of this excitation waveform was chosen within the range 0.002 to 0.05 V, such that ions of interest would gain enough velocity to undergo energetic collisions with background gas (air 9.5×10^{-5} to 2.8×10^{-4} Torr, corrected ion gauge reading) but have insufficient energy to be immediately ejected from the trap. All chemicals were

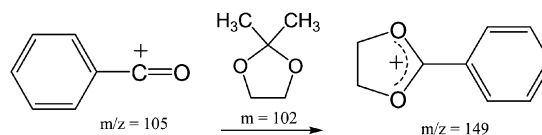
obtained from Sigma-Aldrich (Milwaukee, WI, USA) and were introduced as headspace vapors at ambient temperature from the neat liquids or solids using a variable leak valve (Granville-Phillips, series 203, Helix Technology, Mansfield, MA, USA). Reagent partial pressures were typically 2×10^{-5} Torr (uncorrected, model 354 Bayard-Alpert ion gauge, Granville-Phillips, Helix Technology, Mansfield, MA, USA).

Results and discussion

(1) Eberlin reaction of the benzoyl, 2,2-dimethyl oximinium, and 2,2-dimethyl thiooximinium cations with 2,2-dimethyl-1,3-dioxolane

The benzoyl ion, created by methyl loss from acetophenone, reacted with 2,2-dimethyl-1,3-dioxolane to produce the cycloaddition product, 2-phenyl-1,3-dioxolane, Scheme 1. Evidence for the Eberlin product was obtained by performing a three-stage (MS³) experiment. The reactant ion, benzoyl ion at m/z 105, was isolated by application of a SWIFT waveform (0.05 V amplitude, 235–265 kHz notch, 4 ms), as shown in Fig. 1A. Then all ions observed in the single-stage mass spectrum were ejected from the ion trap except for the ions of interest at m/z 105; in the course of isolating this ion its abundance was attenuated to 75% of the original value. After isolation and a rather long 515 ms reaction period in the presence of 2,2-dimethyl-1,3-dioxolane, the cycloaddition product, 2-phenyl-1,3-dioxolane at m/z 149 was observed (see Fig. 1B). The m/z 149 ion was isolated using a second SWIFT waveform (0.05 V amplitude, 130–170 kHz notch, 4 ms). At this point, all these ions were ejected except for the product ions of interest at m/z 149 which were isolated and subjected to CID (269 ms, 0.01 V, 160 kHz) as the last step of the MS³ experiment. Dissociation yielded two fragments at m/z 87 and 105, with abundances relative to the reactant ion of 31% and 14%, respectively (Fig. 1C). The m/z 105 ion is the product of the well-established reverse-Eberlin reaction.¹⁰ Interestingly the m/z 87 ion is without precedent in the literature. However, literature studies using a triple quadrupole used shorter activation times, typically $\sim 5 \times 10^{-5}$ s residence times, with larger kinetic energies, typically 14–16 eV,²² than those used in these studies. The longer times with lower energies used in these experiments were necessary due to the lower potential well depth of the smaller ion trap.¹⁷ The product ion m/z 87 is believed to be formed by charge exchange of the Eberlin product with neutral 2,2-dimethyl-1,3-dioxolane in the trap, followed by methyl radical loss. This charge exchange is expected to be increasingly favored at low energy and long reaction times such as those used in this study. This reaction is estimated to be slightly endothermic which is consistent with the fact that a large reaction time was necessary to observe it. Nonetheless, the formation of the m/z 87 peak is an interesting dissociation product of the Eberlin reaction since it is an additional structural probe to the formation of the Eberlin product.

An additional MS³ study was performed to characterize the Eberlin cycloaddition product generated in the reaction of 2,2-dimethyl oximinium cation (m/z 72) with 2,2-dimethyl-1,3-dioxolane, a process that yields 2,2-dimethylamine-1,3-dioxolanylium cation at m/z 116. Dissociation of the product ion caused the reverse Eberlin reaction to occur, and thus the only fragment ion observed was m/z 72. To confirm the cyclic



Scheme 1

structure for the Eberlin product, a sulfur atom was substituted for the oxygen in the ionic reagent. In this experiment, the 2,2-dimethyl thiooximinium cation, formed by dimethyl ammonia loss from tetramethyl thiourea, was reacted with 2,2-dimethyl-1,3-dioxolane to produce the Eberlin cycloaddition product. This product has one sulfur and one oxygen atom in the

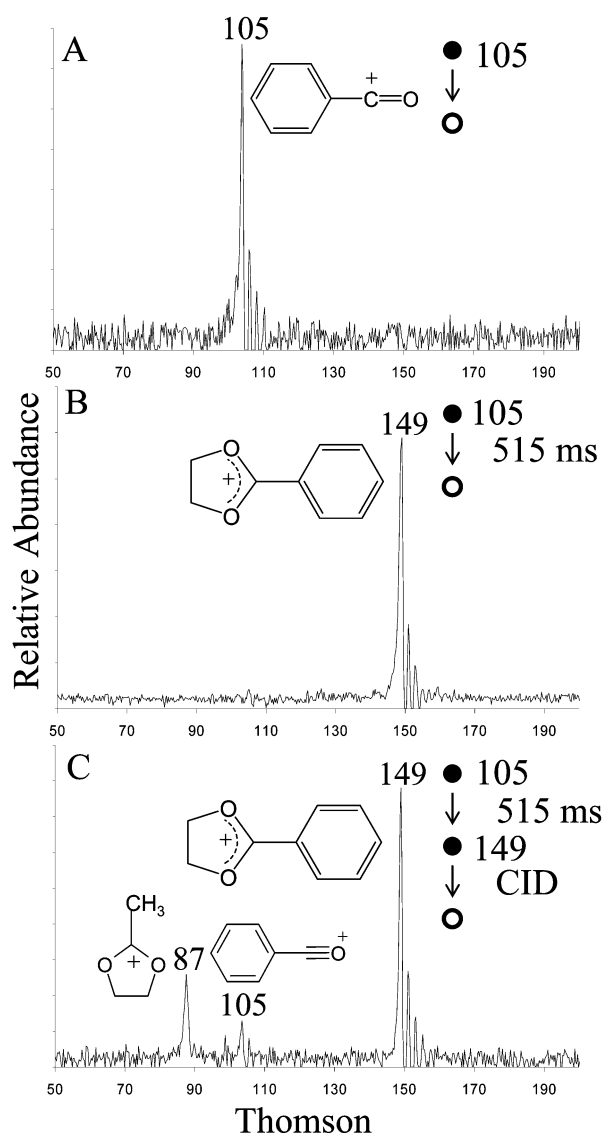


Fig. 1 Evidence for the Eberlin reaction between the benzoyl ion and 2,2-dimethyl 1,3-dioxolane. (A) The benzoyl ion (m/z 105) was isolated by application of a SWIFT waveform (0.05 V amplitude, 235–265 kHz notch, 4 ms). (B) Formation of the product 2-phenyl-1,3-dioxolane (at m/z 149) after 515 ms reaction time. (C) The isolated ion, m/z 149, subjected to CID (269 ms, 0.01 V, 160 kHz) in a MS^3 experiment, yielding two fragment ions, m/z 87 and 105.

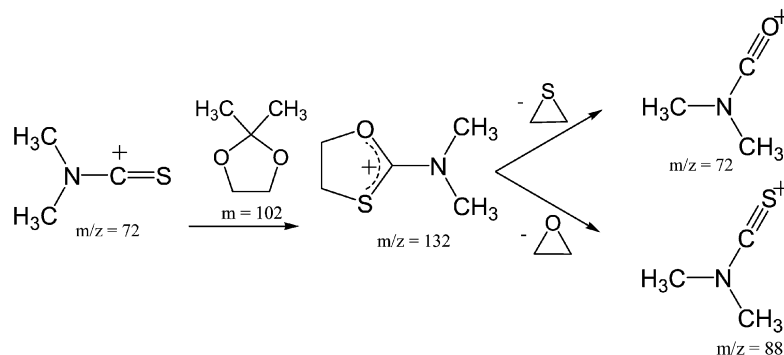
ring, therefore upon dissociation of the cyclic product both the acylium ion and the thio acylium ion should be observed, Scheme 2. In this MS^3 experiment, 2,2-dimethyl thiooximinium cation at m/z 88, was isolated by application of a SWIFT waveform (0.02 V amplitude, 500–600 kHz notch, 4 ms). After isolation and a 200 ms reaction period in the presence of 2,2-dimethyl-1,3-dioxolane, the cycloaddition product at m/z 132 was observed and isolated using a second SWIFT waveform (0.02 V amplitude, 150–250 kHz notch, 4 ms), then dissociated by CID (10 ms, 0.01 V, 200 kHz) as the final step of the MS^3 experiment. Dissociation yielded two fragments at m/z 72 and 88, with abundances relative to the reactant ion of 20% and 30%, respectively (Fig. 2). The m/z 72 ion is the product of fragmentation of the Eberlin reaction product back to the ionic precursor and the m/z 88 ion is the corresponding thio acylium analog.⁶ The formation of the ion at m/z 88 provides evidence for the cyclic structure for the Eberlin reaction product.

(2) Eberlin reaction of phosphonium ion $CH_3P(O)OCH_3^+$ with 1,4-dioxane

The Eberlin reaction was also found to occur between the phosphonium ion $CH_3P(O)OCH_3^+$, m/z 93, formed from the chemical warfare agent simulant dimethyl methylphosphonate (DMMP), and 1,4-dioxane, Scheme 3. Fig. 3 shows a mass spectrum recorded after allowing 515 ms of reaction time (without isolation of the phosphonium ion), demonstrating no observable ion signal at m/z 93 while m/z 125, assigned as protonated DMMP, is the base peak and the Eberlin adduct at m/z 137 is 35% of the base peak. Isolation of the m/z 93 ion followed by a long reaction period did not yield the Eberlin reaction product—presumably because of the excess energy acquired by the ion during the isolation step. A similar observation was made for the methanol addition reaction discussed below.

(3) Meerwein reaction of the ion $CH_3P(O)OCH_3^+$ with propylene sulfide

Meerwein reaction between the phosphonium ion $CH_3P(O)OCH_3^+$, m/z 93, generated from DMMP and both propylene sulfide and oxide was observed (Scheme 4). This reaction allowed structural elucidation of the product by dissociation with loss of either the S or the O atom. Fig. 4A shows a mass spectrum recorded after allowing 200 ms of reaction time (without isolation of the phosphonium ion), demonstrating an observable ion signal at m/z 93 while m/z 125, again assigned as protonated DMMP, is the base peak and the adduct m/z 167 is 70% of the base peak. The adduct ion was then isolated using a second SWIFT waveform (0.02 V amplitude, 120–200 kHz notch, 4 ms), and dissociated by CID (4 ms, 0.02 V, 180 kHz), which yielded fragments at m/z 93 and m/z 109 and m/z 125 (Fig. 4B). The m/z 88 ion is the product of reverse-



Scheme 2

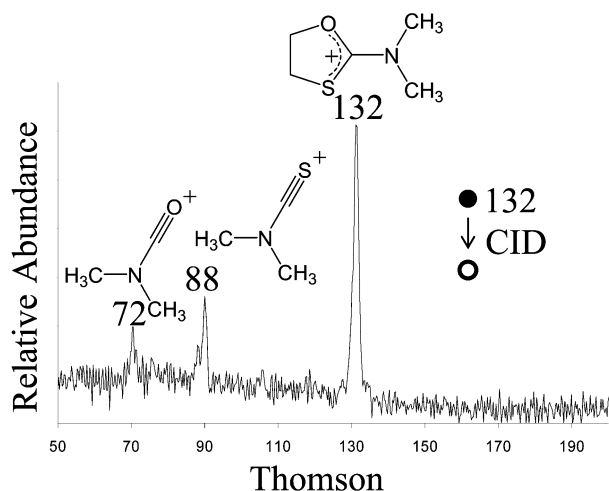


Fig. 2 Collision induced dissociation of the isolated (10 ms, 0.01 V, 200 kHz) 2,2-dimethylamine-1,3-oxathiolanium ion (at m/z 132) produced in the Eberlin reaction between the 1,2-dimethyl thiooximinium ion and 2,2-dimethyl 1,3-dioxolane.

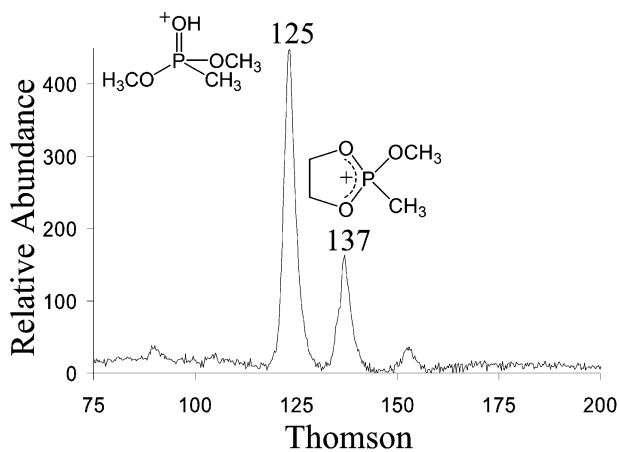
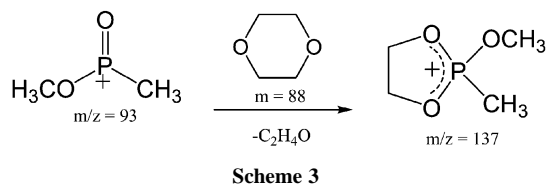
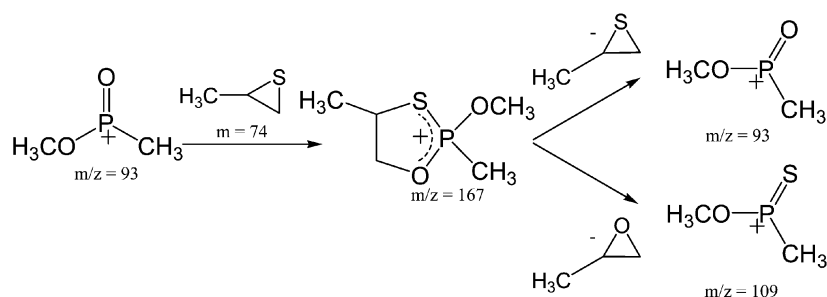


Fig. 3 Mass spectrum (with 515 ms reaction time) showing the Eberlin reaction between phosphonium ion $\text{CH}_3\text{P}(\text{O})\text{OCH}_3^+$ (m/z 93), a fragment of DMMP, and 1,4-dioxane to form product at m/z 137.



Meerwein reaction and the m/z 109 ion is the corresponding thioacylium ion.⁷ The ion at m/z 109 provides evidence for the cyclic structure of the product and can be used for additional selectivity for identification of organophosphorous compounds.

(4) Meerwein reaction of the benzoyl cation with propylene oxide and propylene sulfide

Meerwein ring expansions were performed between the benzoyl ion and both propylene oxide and propylene sulfide. In these MS^2 experiments, the benzoyl ion (m/z 105) was isolated (0.03 V amplitude, 420–480 kHz notch, 4 ms) and reacted (200 ms) with either propylene oxide or propylene sulfide, to form the products, 4-methyl-2-phenyl-1,3-dioxolane at m/z 163 and 4-methyl-2-phenyl-1,3-oxathiolanium at m/z 179 (Scheme 5).

(5) Ketalization of the benzoyl cation with ethylene glycol

The benzoyl ion was reacted with ethylene glycol to produce the ketalization product, 2-phenyl-1,3-dioxolanium cation, Scheme 6. In this MS^2 experiment, the benzoyl ion was isolated (0.03 V amplitude, 420–480 kHz notch, 4 ms) and reacted with ethylene glycol (200 ms) forming the product 4-methyl-2-phenyl-1,3-dioxolanium cation at m/z 149 (see Fig. 5).

(6) Denitration

Nitrobenzene was found to react with benzonitrile radical cations in an addition/ NO_2 elimination sequence to generate an arylated nitrile, $\text{Ar}^+\text{N}\equiv\text{CAr}'$ (where Ar = aryl from nitrobenzene, Ar' = aryl from benzonitrile), Scheme 7. The molecular ion of benzonitrile at m/z 103 was isolated (0.04 V amplitude, 410–540 kHz notch, 4 ms) with 95% retention of the original peak height and was the only peak observed in the isolation mass spectrum, Fig. 6A. With the introduction of a mixture of d_5 - and d_0 -nitrobenzene and allowing 500 ms of reaction time, three peaks were observed in the product ion mass spectrum, m/z 103 (100%), m/z 180 (14%), and m/z 185 (36%). Isolation (0.08 V amplitude, 150–250 kHz notch, 4 ms) of the m/z 185 ion, $\text{C}_6\text{D}_5^+\text{N}\equiv\text{CC}_6\text{H}_5$, was then accomplished without contamination by other ions, Fig. 6B. Isolation of the d_5 -product (m/z 185) was achieved with a SWIFT waveform (200 kHz, 0.02 V amplitude), Fig. 6C. The MS^3 spectrum (200 kHz, 0.02 V amplitude, 200 ms dissociation) showing the collision-induced dissociation of the m/z 185 ion yielded ions of m/z 185 (100%) and m/z 103 (16%), Fig. 6D. It is reported¹⁶ that this dissociation process yielded m/z 152 and 77 in a 1:3 ratio. The formation of the m/z 103 ion, presumably by charge exchange with the neutral benzonitrile in the trap, was facilitated by the long dissociation time and low energy conditions in the reduced size ion trap.

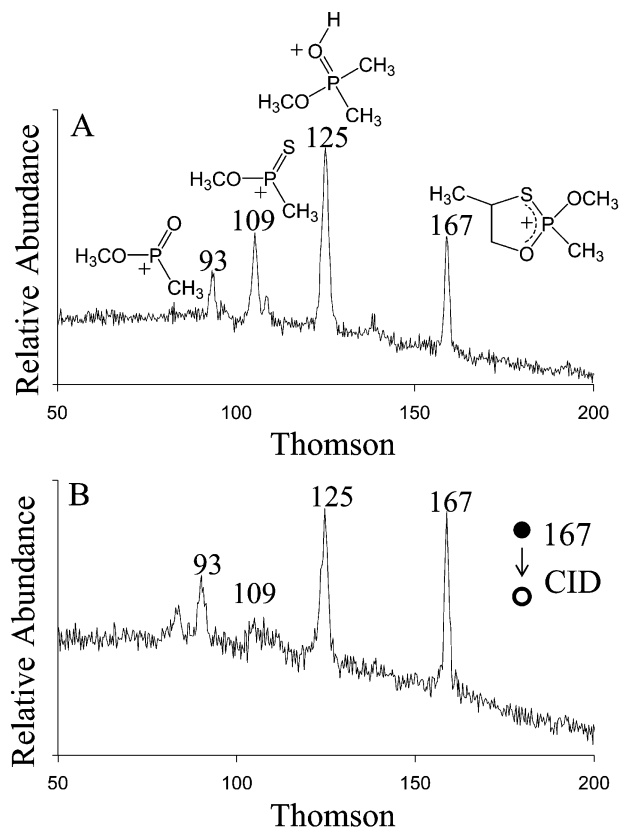
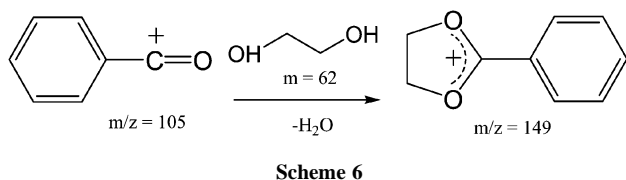
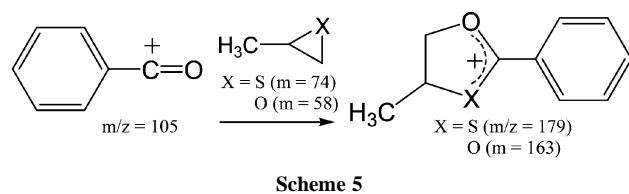


Fig. 4 (A) Mass spectrum (with 515 ms reaction time) showing the Meerwein reaction between phosphonium ion $\text{CH}_3\text{P}(\text{O})\text{OCH}_3^+$ (m/z 93), a fragment of DMMP, and propylene sulfide in the ion trap. (B) CID spectrum of the reaction product (m/z 167), to yield fragments at m/z 93, m/z 109 and m/z 125.



(7) Methanol addition

The C_7H_7^+ ion, formed from NO_2 loss from the molecular ion of *p*-nitrotoluene, was found to react with methanol in a simple addition reaction to form m/z 137, Scheme 8. The reaction products were recorded in Fig. 7, after 11 ms reaction time and 511 ms reaction time. After 11 ms reaction time, the relative abundance of each peak was m/z 91 (94%), m/z 107 (100%), m/z 123 (12%), m/z 137 (69%), while after 511 ms reaction time the relative abundances changed to m/z 91 (7%), m/z 107 (100%), m/z 123 (47%) and m/z 137 (75%)—showing a significant depletion of m/z 91 and increase in m/z 137 while m/z 107 and 123 remained relatively constant. This reaction did not occur when the ion m/z 91 was isolated and this is assumed to be due to excess energy imparted to the m/z 91 ion upon isolation.

The structure of the proposed ion/molecule reaction product—assumed to be protonated *p*-methylanisole (m/z 123), was confirmed by comparison of its CID spectrum with that of an authentic ion of this structure. The authentic ion, protonated *p*-methyl anisole (m/z 123), was formed and isolated (0.05 V, 280–250 kHz notch, and 4 ms duration) in the CIT and then subjected to CID. The CID spectrum of the $[\text{M} + \text{H}]^+$ ion of *p*-methyl anisole yielded m/z 123 (100%), m/z 107 (13%), m/z 91 (15%), whereas the CID spectrum of the reaction product had ion abundances of m/z 123 (100%), m/z 107 (13%), m/z 91 (18%). In both spectra, m/z 107 and 91 are produced in approximately a 1:1 ratio and this agreement strongly suggests that the two ions have the same structure and is consistent with the proposed structure of the product as the simple Lewis acid/base adduct.

The kinetics of the methanol addition reaction was also studied. The reaction was found to be quasi-first order with respect to depletion of m/z 91, C_7H_7^+ with the ion abundance, plotted on a semi-logarithmic scale, showing a slope (k') of 2.7

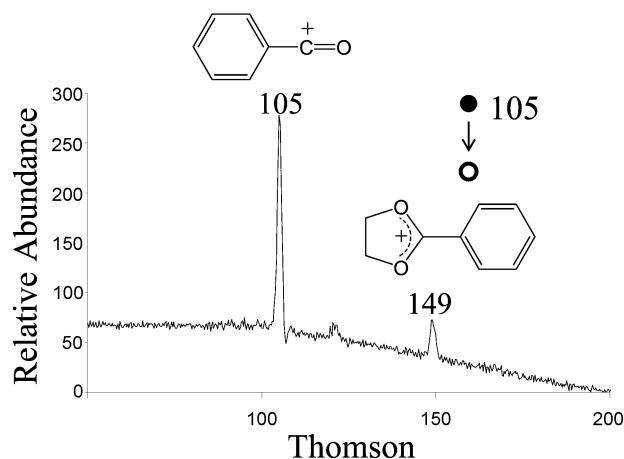
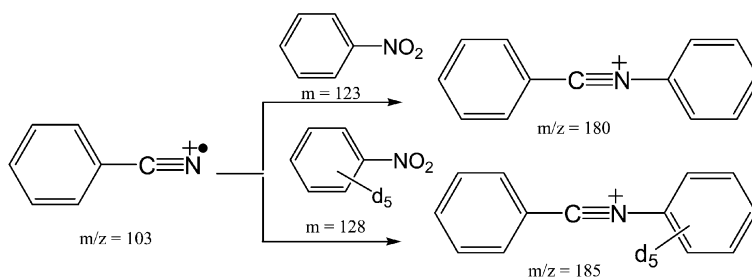


Fig. 5 Ketalization reaction of the benzoyl ion with ethylene glycol. The isolated benzoyl ion (m/z 105) (0.03 V amplitude, 420–480 kHz notch, 4 ms) was reacted for 200 ms with ethylene glycol to form the product 2-phenyl-1,3-dioxolanium cation (at m/z 149).



s⁻¹. The partial pressure of the methanol reactant at the ion gauge was read as 3×10^{-6} torr (uncorrected), corresponding to an estimated number density of 9.7×10^{10} molecules cm⁻³. Assuming the partial pressure of the methanol in the ion trap is the same as that measured at the ion gauge, the rate of the reaction was found to be 2.6×10^{11} cm³ s⁻¹ molecule⁻¹. This is much slower than the expected rate for a simple reaction like this for which a rate greater than 5×10^{10} cm³ s⁻¹ molecule⁻¹ is expected.²³ This difference is believed to be due to the fact that the pressure in the ion trap is lower than that measured at the ion gauge. Assuming that this reaction occurs at the typical rate, this information can be used to calibrate the pressure in the ion trap. Using this method it was determined that the number density of methanol in the trap is actually 1.9×10^{10} molecule cm⁻³ corresponding to a partial pressure of 6×10^{-7} Torr of

methanol in the trap. This is consistent with intuition that the pressure of the reactant would be lower in the trap. The partial pressure of the methanol in the trap gives a calibration of how much sample actually gets into the trap and experiments of this type could be useful for further kinetic studies and for design of sample introduction systems to optimize performance of the instrument for trace analysis.

Conclusions

The MSⁿ capabilities of the miniature mass spectrometer have allowed ion/molecule reactions to be used as structural probes for ions of interest, enhancing the selectivity of the instrument for targeted compounds in field analysis. Cycloaddition of phosphonate and of acylium ions, the NO₂ addition/elimination reaction and the Lewis acid addition are among the ion/molecule reactions that have been performed in a miniature cylindrical ion trap mass spectrometer. Although all the reactions studied are chemically interesting, the Eberlin and Meerwein reactions of the phosphonium ion with 1,4-dioxane and propylene sulfide, respectively, are particularly noteworthy since they may be diagnostic for nerve agent detection. A fragment of *p*-nitrotoluene, C₇H₇⁺ *m/z* 91, was shown to add to methanol and the kinetics of this reaction was qualitatively monitored, and shown to be quasi-first order. Nitrobenzene was reacted with benzonitrile radical cations in an addition/NO₂ elimination process to form an arylated nitrile cation, a reaction that is diagnostic for nitroaromatic explosives. Future directions of the project include testing mixtures of the targeted compounds with common air contaminants to establish the magnitude of matrix effects.

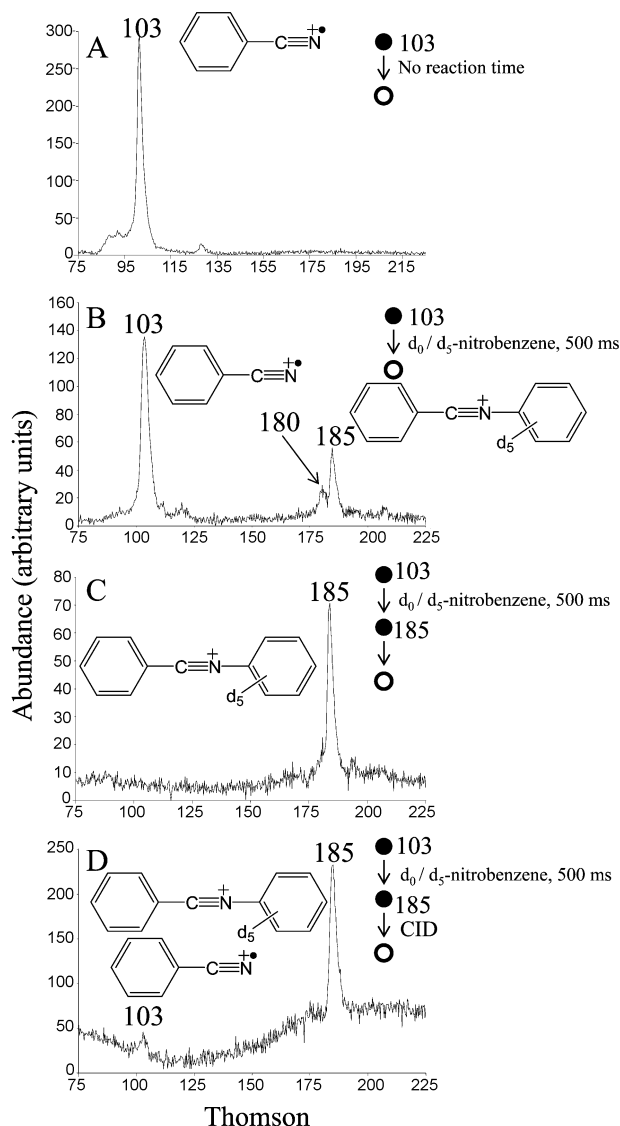
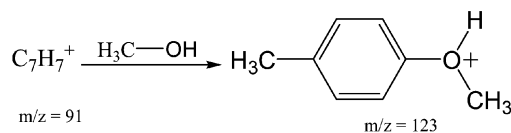


Fig. 6 (A) Isolation (0.04 V amplitude, 410–540 kHz notch, 4 ms) of the molecular ion of benzonitrile (*m/z* 103) (B) Reaction (500 ms) of the isolated benzonitrile with a mixture of d₅ and d₀ nitrobenzene and formation of *m/z* 180 and 185. (C) Isolation (0.08 V amplitude, 150–250 kHz notch, 4 ms) of the *m/z* 185 ion, C₆D₅⁺N≡CC₆H₅ (D) MS³ spectrum.



Scheme 8

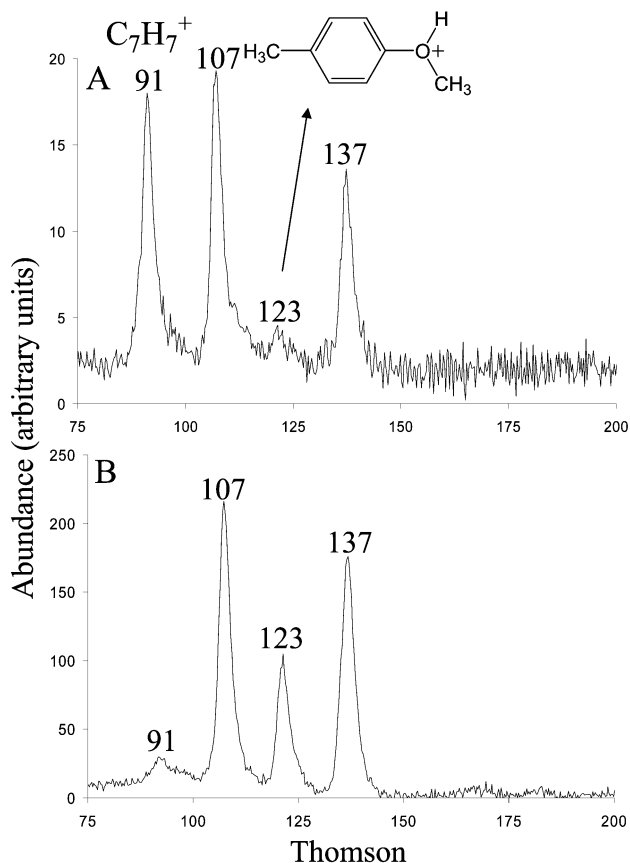


Fig. 7 Mass spectrum showing the addition products of reaction of C₇H₇⁺ (formed from NO₂ loss from the molecular ion of *p*-nitrotoluene) with methanol. Reaction times (A) 11 ms, (B) 511 ms.

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