

Ion/Molecule Reactions for Detecting Ammonia Using Miniature Cylindrical Ion Trap Mass Spectrometers

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SUPPLEMENTARY MATERIAL

KEYWORDS: miniature mass spectrometer, environmental monitoring, ion/molecule reactions, glow discharge electron ionization source, ambient conditions, sorbent trap, gas monitoring

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Summary

The contents of this Supplementary Material section are outlined in parallel to the main text for easy reference. Included is a more detailed explanation of the sample preparation and introduction system; single stage and ammonia reaction mass spectra for bromobenzene, bromobenzene-d₅, chlorobenzene, and 1,2,4-trichlorobenzene; and mass spectrum for the two nitrile reactions that were explored.

Experimental

Sample preparation and introduction system

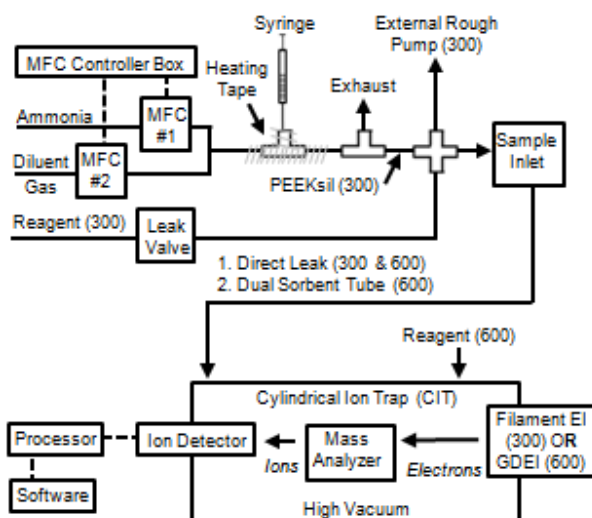


Figure 1 Schematic of the sample preparation and introduction systems

The sample introduction system is pictured in Fig. S1. Gaseous ammonia was introduced using a gas-phase sample introduction system composed of two mass flow controllers (MFCs; MKS Instruments, Andover, MA; Teledyne Hastings Instruments, Hampton, VA) fitted with Teflon tubing (0.6 cm diameter; Swagelok, Indianapolis, IN) and stainless steel ferrules and nuts (Swagelok). OSHA D breathable compressed air was used to dilute the analyte to produce

concentrations ranging from low-ppm to the maximum concentration of the ammonia cylinder (503 ppm). Gas regulators (Air Liquide) delivered the gas directly to the MFC and controlled the pressure of the gas while a controller box specific for the MFC manufacturer was used to control gas flow. The back-end of each MFC was connected to a series of Teflon tubing and stainless steel unions (Swagelok), as depicted.

A section of apparatus was added to the sample introduction system to study the chemical kinetics of 1,2-dichlorobenzene molecular radical cation with ammonia and two amines (methylamine and ethylamine). For these experiments, liquid methylamine and ethylamine were delivered separately *via* syringe (Hastings 81165, 250 μL , 3.26 mm diameter) at a heated ($\sim 90^\circ\text{C}$) Teflon tee (Swagelok) into a steady stream of the ammonia gas standard (503 ppm at 100 mL/min) at a constant rate using a syringe pump (Harvard Apparatus). The rate at which pure methylamine [formula weight (FW) 31.060 g/mol; density 0.902 g/mL; flow rate 4.26 $\mu\text{L/hr}$] and ethylamine (FW 45.080 g/mol; density 0.810 g/mL; flow rate 6.88 $\mu\text{L/hr}$) were introduced was such that a simple calculation estimated an overall concentration of about 503 ppm for ammonia and the two amines.

For direct air leak experiments on the Griffin 300, PEEKsil (length 10 cm, inner diameter 50 μm , SGE, Inc., Austin, TX) was used to insure a constant, restricted flow of the analyte gas stream to the stainless steel union at which headspace vapors above a neutral reagent compound (Griffin 300 only) were introduced by leak valve (Granville-Phillips, Series 203). This restricted flow was necessary to keep the pressure of the Griffin 300's manifold low ($\sim 2 \times 10^{-4}$ Torr) during direct leak experiments because it does not have a valve at the inlet to open and close when sample is introduced or a sample pump like in the ChemSense 600. In fact, this PEEKsil capillary should provide an identical pressure regime inside the ion trap of the Griffin 300 and

ChemSense 600 because it was the same as that used in the ChemSense 600 for direct leak experiments, which also allowed for easy transfer of this technique to the ChemSense 600.

When using the ChemSense 600, headspace vapor of the reagent was introduced directly to the vacuum chamber *via* a glass finger tube and solenoid valve set-up normally used for the instrument's PFTBA mass calibrant. This union was also directly connected to an external roughing pump, used only to initially evacuate the sample introduction system of atmospheric air on the Griffin 300 and the sample inlet of the instrument that fed the neutrals to the instrument's CIT where they were ionized.

The ChemSense 600's dual sorbent tube sample inlet system was used here to pre-concentrate low gas phase concentrations of ammonia. Sample was collected onto the sorbent tube bedding for a sampling time period of 30 s. The tube was opened to the vacuum chamber after 3 s, which gave enough time for the valves to switch on and off fully. After this time, the mass spectrometer started scanning using the custom reaction scan function, as described in detail below (Fig. 1) for the next 40 s (unless otherwise noted for a special case). While this was occurring, residual air in the tube was evacuated (10 s), sample was desorbed from the sorbent material by heating (150°C for 20 s), and the heater was turned off so that the tube could cool (10 s) for the remainder of the mass scan. The sorbent tube method was 73 s total in length.

The effective sample flow rate into the vacuum chamber of the Griffin 300 was fixed at 0.25 mL/min using the PEEKsil capillary with a partial pressure in the vacuum chamber of 6×10^{-5} Torr to 8×10^{-5} Torr. For comparison purposes, the direct leak flow for the ChemSense 600 is 0.1 L/min and the sorbent trap sampling flow rate for the ChemSense 600 is 0.5 L/min. Although both analyte and the precursor neutral headspace gas flow through the same lines,

reaction of the neutrals is not expected because neutral-neutral reaction rate constants are generally about 3 orders of magnitude smaller than ion/molecule reaction rate constants.

In the special case where acetonitrile, benzonitrile, and aqueous ammonia headspace were introduced, sampling took place directly at the PEEKsil capillary on the Griffin 300 or directly at the sample inlet on the ChemSense 600.

Results and discussion

Halobenzenes as reagents in ion/molecule reactions with ammonia

Single stage mass spectrum were recorded for all five halobenzene species (bromobenzene, bromobenzene- d_5 , chlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene) as well as spectra for the ammonia reaction. Fig. S.2 shows the scan function used for a single stage mass spectrum. Fig. S.3 through S.6 show mass spectra for four of the halobenzene species, where 1,2-dichlorobenzene can be found in Fig. 2.

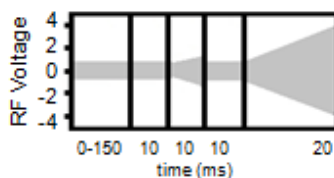


Figure S.2. Graphical depiction of the single stage scan function. The segments were: 1) ionization: duration for this step was variable and controlled by the instrument's automatic level control (ALC) algorithm, 2) ion cooling, 3) RF ramp from m/z 50 up to 75 to remove low-mass ions that may not be properly ejected in step 5, 4) ion cooling: LMCO returned to m/z 50, and 5) RF ramp for mass analysis from m/z 50 to 300.

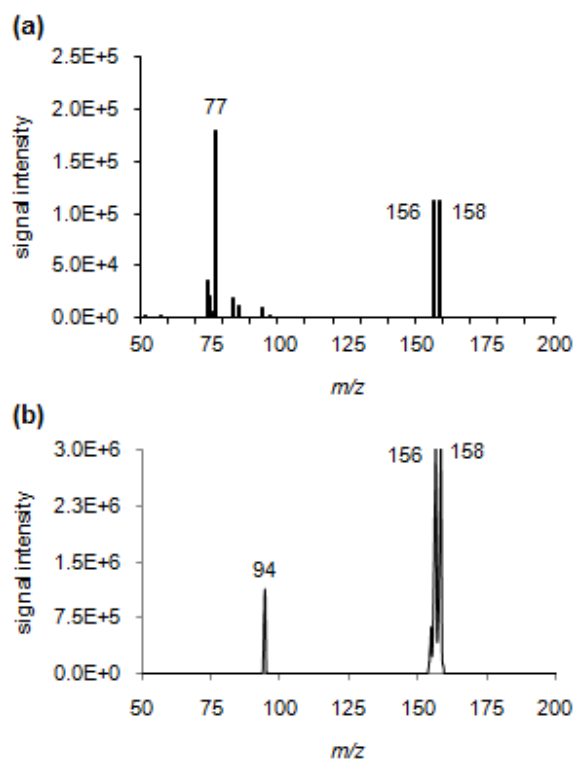


Figure S.3. **a)** Single stage mass spectrum of bromobenzene (monoisotopic peak, m/z 156 $C_6H_5Br^+$; m/z 77 $C_6H_5^+$) using the scan function shown in Fig. S.2. **b)** Bromobenzene cations (m/z 156 and 158, the isotopic signature) and the product (m/z 94 $C_6H_5NH_3^+$) of their ion/molecule reaction with headspace vapor over aqueous ammonia solution. (Direct leak, Griffin 300)

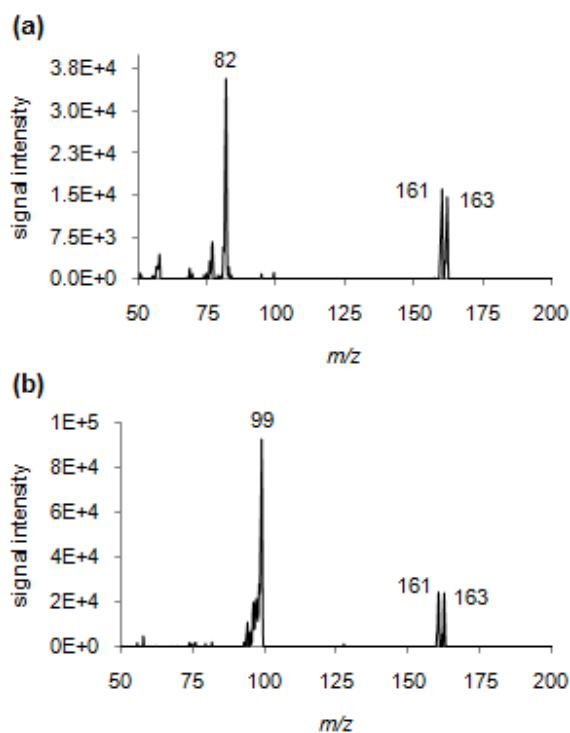


Figure S.4. **a)** Single stage scan mass spectrum of bromobenzene- d_5 (monoisotopic peak, m/z 161 $C_6D_5Br^+$; m/z 82 $C_6D_5^+$) using the scan function shown in Fig. S.2. **b)** Bromobenzene- d_5 cations (m/z 161 and 163, isotopic signature) and the product (m/z 99 $C_6D_5NH_3^+$) of their ion/molecule reaction with headspace vapor over aqueous ammonia solution. The peaks at lower mass to m/z 99 are possibly from H/D exchange. The shift of five mass units for all three ions (vs. Fig S.3) is consistent with perdeuteration of the benzene ring. (Direct leak, Griffin 300)

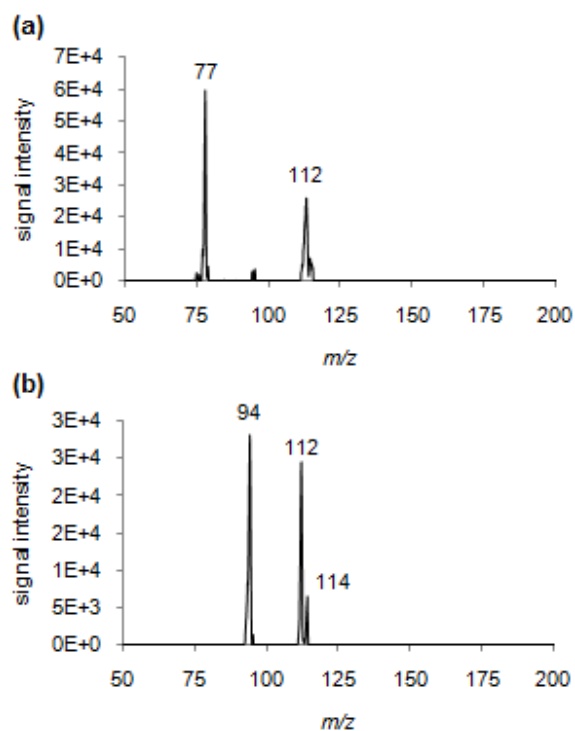


Figure S.5. **a)** Single stage scan mass spectrum of chlorobenzene (monoisotopic peak, m/z 112 $C_6H_5Cl^+$; m/z 77 $C_6H_5^+$) using the scan function shown in Fig. S.2. **b)** Chlorobenzene cations and the product (m/z 94 $C_6H_5NH_3^+$) of their ion/molecule reaction with headspace vapor over aqueous ammonia solution. (Direct leak, Griffin 300)

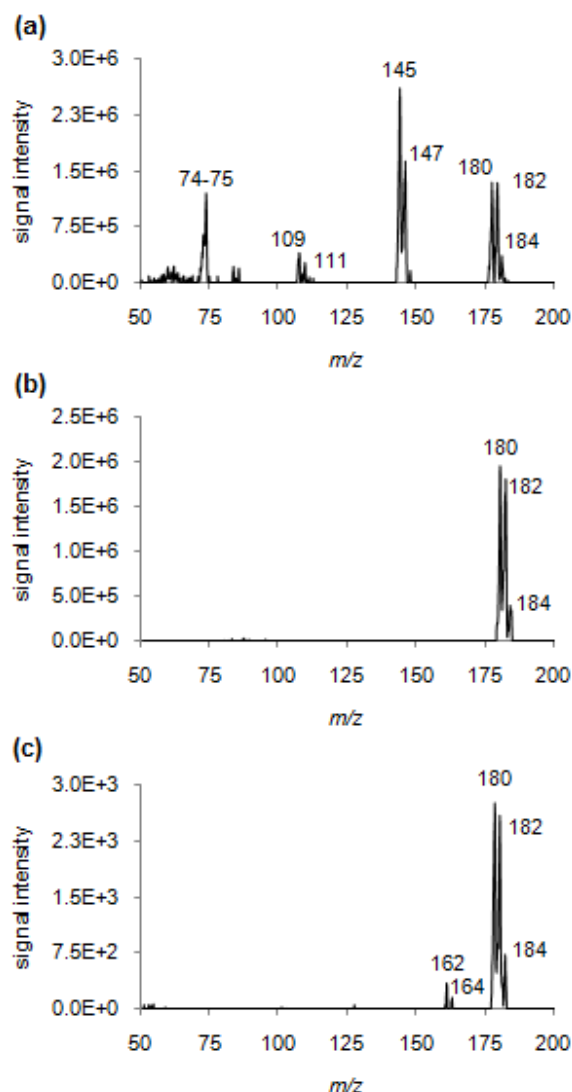


Figure S.6. **a)** Single stage scan mass spectrum of 1,2,4-trichlorobenzene (monoisotopic peak, m/z 180 $C_6H_3Cl_3^+$) using the scan function shown in Fig. S.2. The molecular peaks are at m/z 180, 182, and 184, with the fourth chlorine isotope peak at m/z 186, $C_6H_3^{37}Cl_3^+$, not observed, although expected at only 1.5% relative abundance. Other peaks include: $C_6H_2^+$ at m/z 74, $C_6H_3^+$ at m/z 75, and, consistent with the chlorine isotope signature, $C_6H_2Cl^+$ at m/z 109 and m/z 111, and $C_6H_3Cl_2^+$ at m/z 145 and 147. **b)** Isolation of the molecular ion of 1,2,4-trichlorobenzene (m/z 180); isotopomeric ion peaks shown. The main ions ejected during this step were $C_6H_2^+$ at m/z 74, $C_6H_3^+$ at m/z 75, $C_6H_2Cl^+$ at m/z 109, and $C_6H_3Cl_2^+$ at m/z 145, as contrasted with (a). **c)** Mass spectrum of 1,2,4-trichlorobenzene reacting with ammonia (503 ppm) where the reaction scan function (Fig. 1) was modified to have a LMCO just below the molecular ion peak (m/z 180 $C_6H_3Cl_3^+$) for 800 ms of PIAT and ions over m/z 50 were collected. The molecular ion peak at (m/z 180 and 182) and the peaks that result from reaction with ammonia (m/z 162 $C_6H_3Cl_2NH_3^+$), consistent with the isotopic signature for the two chlorine atoms left on the benzene ring, are observable. (Direct leak, Griffin 300)

Assessment of competing reaction paths

A plot comparing normalized product ion signal vs. the PIAT for a PIAT LMCO of m/z 50 and 125 for the reaction of 1,2-dichlorobenzene with ammonia is shown in Fig. S.7.

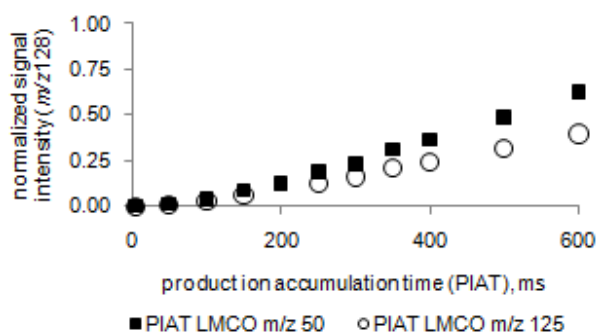


Figure S.7. A plot comparing normalized product ion signal (m/z 128 $C_6H_4ClNH_3^+$) with respect to total ion signal vs. PIAT for a PIAT LMCO of m/z 50 and 125 for the reaction of 1,2-dichlorobenzene with ammonia. (Direct leak, Griffin 300)

Reaction of 1,2-dichlorobenzene with ammonia and two amines

1,2-Dichlorobenzene was reacted with ammonia, methylamine, and ethylamine (all at 503 ppm) in the gas phase as described in the experimental section. The expected product ions formed for methylamine (m/z 142 $C_6H_4ClNH_2CH_3^+$) and ethylamine (m/z 156 $C_6H_4ClNH_2CH_2CH_3^+$) presumably follow a reaction analogous to reaction 1 (Fig. S.8). The product ion signal for ammonia and the two amines and for the monoisotopic peak of 1,2-dichlorobenzene (m/z 146) were normalized to the total signal for all species in the trap. These values were plotted against PIAT to obtain a relative reaction rate plot for the three amines.

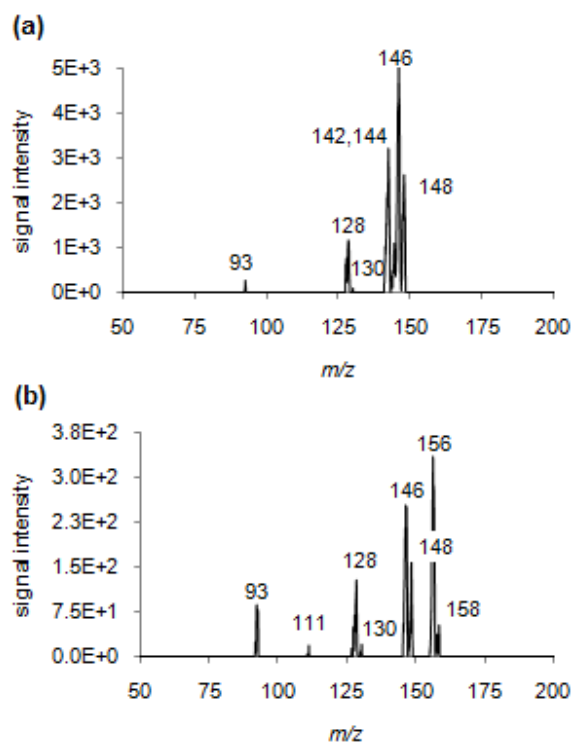


Figure S.8. Mass spectrum of 1,2-dichlorobenzene reacting with a mixture of ammonia (503 ppm) and either **a)** methylamine (503 ppm) or **b)** ethylamine (503 ppm). Molecular ion peaks for 1,2-dichlorobenzene (m/z 146 $C_6H_4Cl_2^+$) and the peaks that result from its reaction with ammonia (m/z 128 $C_6H_4ClNH_3^+$), methylamine (m/z 142 $C_6H_4ClNH_2CH_3^+$), and ethylamine (m/z 156 $C_6H_4ClNH_2CH_2CH_3^+$) where the isotopic signature of chlorine is evident are shown. Fragment ions were present at m/z 111 ($C_6H_4Cl^+$) and m/z 93 ($C_6H_4NH_3^+$) for low PIAT times in some spectra. Both spectrum were acquired using the reaction scan function (Fig. 1) with a PIAT 200 ms and the ionization time held constant at 150 ms. (Direct leak, Griffin 300)

Nitrile reactions

Reaction of 1,2-dichlorobenzene with acetonitrile Fig. S.9 shows the mass spectrum for the reaction of 1,2-dichlorobenzene with acetonitrile.

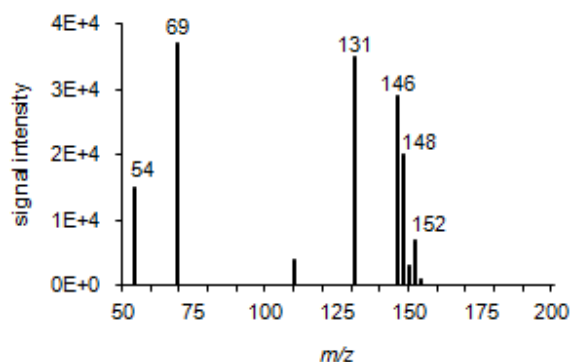


Figure S.9. Mass spectrum showing results of an (inadvertent) ion/molecule reaction between the 1,2-dichlorobenzene radical cation (m/z 146 and 148) and acetonitrile (CH_3CN). The product ion at m/z 152 corresponded to $[\text{C}_6\text{H}_4\text{CINCCCH}_3]^+$, and the minority isotopic peak for chlorine is seen at m/z 154, although not at a level consistent with the expected 3 to 1 ratio. Ions at m/z 69 and 131 correspond to residual perfluorotributylamine (PFTBA) mass calibrant in the trap. (Direct leak, ChemSense 600)

Reaction of a pseudohalogenide with ammonia Fig. S.10 shows the mass spectrum for the reaction of benzonitrile, a pseudohalogenide, with ammonia.

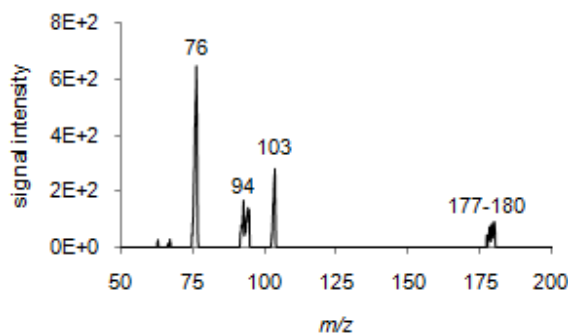


Figure S.10. Mass spectrum showing results of an ion/molecule reaction between benzonitrile, a pseudohalogenide, headspace ($\text{C}_6\text{H}_5\text{CN}$; FW 103 g/mol; $\sim 1,300$ ppm) and aqueous ammonia headspace ($\sim 700,000$ ppm). The peak cluster at m/z 94 corresponds to the expected product ion ($\text{C}_6\text{H}_5\text{NH}_3^+$) while that at m/z 76 is C_6H_4^+ . An interesting cluster of peaks was found in the m/z 177–180 region. Though the identity of these species is uncertain, the cluster does appear to be from the reaction of benzonitrile with ammonia since it was only present when both ammonia and benzonitrile were reacting in the trap. (Direct leak, Griffin 300)