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Selective detection of gas-phase aldehydes and ketones using protonated hydrazine

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Abstract

This article reports the results of the gas phase studies of protonated hydrazine, $N_2H_5^+$, reactions with different classes of organic compounds in a chemical ionization mass spectrometer (CIMS). We found that saturated aldehydes react with $N_2H_5^+$, in the presence of a drift field and neutral hydrazine, to form primarily a protonated hydrazone, e.g. formaldehyde reacts to form $CH_2N_2H_3^+$. Unsaturated aldehydes, saturated ketones, and hydroxyl substituted carbonyl compounds react to form protonated hydrazones and association complexes, e.g. $N_2H_5^+ \cdot$ acetone. In the absence of a drift field, methanol, ethanol, and toluene react to form association complexes; otherwise, no reaction occurs. We propose a method of detecting gas-phase aldehydes and ketones using protonated hydrazine, $N_2H_5^+$, as a reagent ion in a CIMS. The method was demonstrated by measuring three C_6 aldehydes released by grass that had been frozen, crushed and thawed. Qualitatively and quantitatively, the results compare favorably with the results of aldehyde emission experiments reported by others. (Int J Mass Spectrom 210/211 (2001) 503–509) © 2001 Elsevier Science B.V.

Keywords: Gas phase ion chemistry; Aldehyde and ketone detection; Protonated hydrazine; Plant emissions

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1. Introduction

Speciation and quantification of carbonyl compounds, aldehydes, and ketones, in the atmosphere are crucial to determining volatile organic compound (VOC) emission inventories, evaluating air quality models, and understanding photochemical air pollution. Carbonyls are released directly into the atmosphere or formed as moderately stable intermediate products of the oxidation of other VOCs. Carbonyl compounds are further oxidized through reactions initiated by photolysis or reactions with hydroxyl radicals. Measurement of carbonyl species in indoor air is also important due to their low odor and irritation thresholds [1]. Current methods of measuring carbonyl species typically involve trapping, concentrating, and sometimes derivitization. These methods usually require several steps and are integrative. Evidence of ozone interference during sampling on 2,4-dinitrophenylhydrazine (DNPH) cartridges has prompted researchers to put prefilters on sampling systems [2,3], potentially skewing results. Methods using Tenax as a sorption/desorption medium are also troubled by ozone interferences [4,5].

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Dedicated to Professor Nico Nibbering on the occasion of his retirement.

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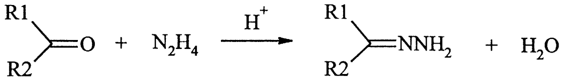
Chemical ionization mass spectrometry (CIMS) has been exploited in recent years to overcome some of the limitations of traditional trace organic measurement methods [6–9]. One of the more successful forms of CIMS for atmospheric applications is the proton-transfer reaction mass spectrometer (PTR-MS) [10]. In this device, protons are transferred from a reagent ion (e.g. H_3O^+) to the organic compound (the analyte), ionizing the analyte for subsequent mass filtering and detection. An electric field is used to raise the effective kinetic temperature of the ions and thus inhibit the formation of water clusters. The response time of the instrument, of the order of a second, is limited simply by the residence time of the sampling system. Detection limits for some organic compounds have been reported in the low parts per trillion range [10]. It is also selective: proton transfer only occurs where the proton affinity (PA) of the analyte is higher than that of the precursor to the reagent ion (e.g. H_2O). Thus organic compounds, with a greater PA than H_2O (724 kJ mol^{-1}) can be measured, whereas most other air components (O_2, N_2, CO_2, etc.), which have lower PAs, will not be detected.

Proton transfer to many organic compounds (e.g. most alkanes and alkenes) is nondissociative. However, dissociation occurs for the proton transfer products of aldehydes and alcohols [11–13]. In some cases, the pattern of dissociation can assist in identification of the compound. In other cases, this dissociation can produce ions that coincide with those identified with other compounds. For example, H_3O^+ proton-transfer reactions, in an electric field, with 3-hexenyl acetate, 2-hexenol, and hexanal all result in major identifying product ions at *m/z* 55 and 83 [13]. These three compounds, and many others, are released from plant material that has been damaged and exposed to air [14]. Combining PTR-MS results with measurements from a second CIMS apparatus using a different reagent ion may allow identification of some of these difficult to segregate analytes. One promising reagent ion is NO^+, which reacts with aldehydes and ketones to make unique ions and may make it possible to distinguish some carbonyl isomers [11,12].

To identify a reagent ion that would be selective for carbonyl compounds, but would not react rapidly with other species in air, we looked to the solution phase literature. Solution phase reactions of hydrazine and functionalized hydrazine with carbonyls have been studied for over a century. Fischer used phenylhydrazine to identify aldehydes as far back as 1884 [15], and DNPH was used by Purgotti in 1894 to quantify carbonyls [16]. Hydrazine and its derivatives react with carbonyls by attacking the carbonyl carbon, forming a hydrazone and eliminating water. The reaction is acid catalyzed:



Scheme 1.

To determine if similar chemistry could be useful for identification of carbonyls in a CIMS, we qualitatively assessed the products of the reactions of $N_2H_5^+$ with a variety of organic compounds. From these observations, we developed a method for carbonyl detection and quantification using $N_2H_5^+$ as the reagent ion in our CIMS. The method was then used to detect several aldehydes released when blades of grass are wounded. We then compared our results to previous measurements of wounded plants studied using PTR-MS. Further analysis of rates and mechanisms will be addressed in a separate article [17].

2. Experimental

Because our CIMS instrument has been described in detail elsewhere [7], we present only a brief description of the method and experimental details. The instrument (see Fig. 1) has a flow tube reaction length of 53 cm and an inner diameter of 5.8 cm. It contains an ion drift tube, consisting of a stack of 50 stainless steel rings (0.8 cm width×3.6 cm i.d.) connected by resistors. A dc voltage was applied over the stack of drift rings, resulting in a homogeneous electric field ranging from 20 to 35 V cm^{-1}. The drift field dissociates weakly bound clusters including the hydrazine ion clusters ($N_2H_5^+(N_2H_4)_n$). The vapor over liquid anhydrous hydrazine was metered and

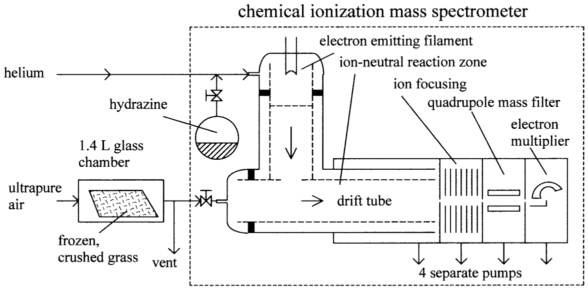


Fig. 1. Schematic of chemical ionization mass spectrometer. Sample air is pumped through a reaction chamber by a mechanical pump. $N_2H_5^+$ ions are formed in the side arm by electron impact ionization of a He/N_2H_4 mixture. Carbonyl compounds in the sample stream react with $N_2H_5^+$, in the presence of N_2H_4, in the drift tube section. Product ions are then mass selected by the quadrupole mass filter and detected by the conversion dynode electron multiplier.

mixed with helium carrier gas. This mixture was injected into the sidearm, upstream of a resistively heated filament. $N_2H_5^+$ ions were formed in the side arm by reactions following electron impact ionization of the He/N_2H_4 mixture. Carbonyl compounds in the sample stream reacted with $N_2H_5^+$, in the presence of N_2H_4, in the drift tube section. Product ions were then mass selected by a quadrupole mass filter and detected by a conversion dynode electron multiplier.

For qualitative determination of the products of the reaction of $N_2H_5^+$ with pure compounds, the CIMS was operated under the following conditions. The pressure in the reaction zone was maintained at 1.4 Torr. The electron-impact ion source operated at a potential of 40 V and electron emission current of 250 μA. For determining product ion speciation, we operated the CIMS in drift tube mode, applying a drift field of 20 V cm^{-1}. A helium flow of 10 STP $cm^3\ s^{-1}$ was used as the reagent ion carrier gas. The flow rate of hydrazine was adjusted to maximize the $N_2H_5^+$ signal. This flow rate was not measured, but was estimated to be ~0.01 STP $cm^3\ s^{-1}$. Approximately 5 STP $cm^3\ s^{-1}$ of nitrogen (the sample flow), containing the analyte, flowed into the reaction zone through a Teflon metering valve.

The following compounds were introduced into the analyte gas stream by diluting the vapor over the pure liquid compound with nitrogen: 2-hexenal, 3-hexenal, octanal, nonanal, *t*-2-nonenal, 2,4-nonadienal, benzaldehyde, hydroxyacetone, 2-pentanone, 3-pentanone, 2-hexanone, 5-hydroxy-2-pentanone, heptane, toluene, methanol, ethanol, 2-methyl-3-butene-2-ol, 3-hexenol, and acetic acid. Formaldehyde was introduced into the sample stream by packing a small amount of paraformaldehyde into a glass tube, flowing N_2 at 0.6 STP $cm^3\ s^{-1}$ through the tube and heating the tube with a heat gun. The following compounds were analyzed by injecting a small amount of the pure liquid into a 100 mL glass bulb and allowing the vapor to diffuse into the analyte gas stream: acetaldehyde, propanal, 2-propenal (acrolein), 2-methyl-2-propenal (methacrolein). Glyoxal (40% aqueous solution) and glycolaldehyde (solid powder) were placed in a vial connected to the diluent gas stream and heated to introduce vapor into the analyte stream. Several compounds were introduced into the sample stream by allowing a regulated (but not quantified) flow of gas from a calibrated gas mixture to mix with the sample stream. The compressed gas mixture contained 1 ppm (parts per million) of each of these compounds in dry air: acetaldehyde, acetone, 2-butanone, 3-methyl-2-butanone, 2-pentanone, 3-pentanone, 5-hydroxy-2-pentanone, 3-hexanone, and chloroacetone, bromoacetone.

All compounds used in this study were obtained from Sigma-Aldrich, except paraformaldehyde, which was obtained from Fisher Scientific, and 3-hexenal, which was obtained from Bedoukian Research Inc. The cylinder of calibration gas was prepared by Apel-Reimer Environmental.

An experiment was performed to detect the release of aldehydes from grass. We obtained the wide-bladed grass (species unidentified) outside of the David Skaggs Research Center in Boulder, CO in January 2001. The grass sample, weighing ~5 g, was frozen in liquid nitrogen and crushed lightly in a mortar. This frozen material was placed in a 1.4 L glass chamber (see Fig. 1). The chamber was ventilated with 18 STP $cm^3\ s^{-1}$ of ultra-pure air. A fraction of the chamber exhaust air was drawn into the CIMS for analysis.

For this wounded grass experiment, the CIMS was operated under the following conditions. Sample intake air flow rate was 16 STP $cm^3\,s^{-1}$. Helium, flowing at 3.5 STP $cm^3\,s^{-1}$, was introduced upstream of the ion source (operated as outlined earlier). The reaction chamber was operated at 1.4 Torr and a drift field of 34 V cm^{-1} was applied.

To obtain quantitative emission rates of C_6 aldehydes from grass, we prepared calibration sources of hexanal, 2-hexenal, and 3-hexenal in separate Tedlar bags. For example, to make a 1 ppm bag sample, 125 μL of 95% pure, liquid hexanal was first mixed with 5 ml of liquid hexane. Then 10 μL of this mixture was injected into a 56 L Tedlar bag. The Tedlar bag was then inflated with air to its maximum capacity and allowed to equilibriate for several hours to ensure even mixing. Adsorption to the walls of the bag and fittings could reduce the effective bag concentration. To minimize this problem, we conditioned the inner bag surfaces by repeating the above mentioned procedure three or more times and at the same time deflating the bag between fills.

3. Results

In the electron impact ionization of the He/N_2H_4 mixture, $N_2H_5^+$ was the major positive ion formed in the ion source region, but several other ions were also detected. Ion signals of the monomer, $N_2H_5^+$, the dimer, $(N_2H_4)_2H^+$, and the trimer, $(N_2H_4)_3H^+$, were of the same order of magnitude, but the presence of a drift field of 20 V cm^{-1} reduced the amount of the dimer by a factor of 100 and the amount of trimer was insignificant. The flow rate of hydrazine was not measured, but was adjusted to optimize the $N_2H_5^+$ signal. A small amount of $N_2H_5^+ \cdot H_2O$ also forms in the absence of a drift field. Under conditions where water vapor was present in the system, little H_3O^+ was present, because the proton affinity (PA) of N_2H_4 (865 kJ mol^{-1}) [18] is much greater than that of H_2O (724 kJ mol^{-1}) [19]. Other ions formed in the ionization of hydrazine include NH_3^+, NH_4^+, and $N_2H_4^+$, but under operating conditions they represent less than 1% of the total ion signal.

3.1. Experiments with gas standards

3.1.1. Aldehydes

Formaldehyde, acetaldehyde, propanal, octanal, and nonanal reacted with $N_2H_5^+$, in the presence of excess hydrazine, to form an ion with a mass equivalent to the protonated hydrazone and no other detectable products, e.g. for formaldehyde:

$$N_2H_5^+ + CH_2O \xrightarrow{N_2H_4} CH_2N_2H_3^+ + H_2O$$

Scheme 2.

The unsaturated aldehydes, 2-propenal, 2-methyl-2-propenal, *t*-2-nonenal, and 2,4-nonadienal, reacted to form the protonated hydrazone but also formed a product with a mass equivalent to that of the association complex, e.g. for 2-nonenal:

$$N_2H_5^+ + C_6H_{13}CH{=}CHCHO \longrightarrow$$
$$N_2H_5^+ \cdot C_6H_{13}CH{=}CHCHO$$

Scheme 3.

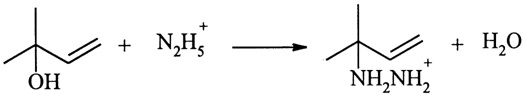
The products of the reaction of 2-hexenal were dominated by the association product, while the hydrazone was the dominant product of the reaction with 3-hexenal. Benzaldehyde reacted similarly, producing both products. The hydroxyl substituted carbonyl compound, glycolaldehyde formed mostly the association product. The only compound containing two carbonyl groups, glyoxal, reacted to form four distinct products: a protonated single hydrazone, $CHOCN_2H_3^+$; a protonated double hydrazone, $H_2N_2CCN_2H_3^+$; a single association product, $N_2H_5^+ \cdot CHOCHO$; and an association product containing a second hydrazine molecule, $N_2H_5^+ \cdot CHOCHO \cdot N_2H_4$. Both of the products containing two hydrazine molecules are likely formed by the reaction of the previous ion product, the adduct or protonated hydrazone, with a second, neutral, hydrazine molecule. Excess neutral hydrazine is present in the ion source and reaction zone and was shown in a more detailed study [17] to be involved in hydrazone formation.

3.1.2. Ketones

The following ketones reacted with $N_2H_5^+$ to form the protonated hydrazone and the association complex: acetone, 2-butanone, isomers of pentanone, 3-hexanone. Qualitatively, these reactions favor the association complex products over the hydrazone. Hydroxyacetone formed primarily the association product whereas 5-hydroxy-2-pentanone formed mostly the hydrazone. No products were observed for reactions of the halogenated ketones, from the calibrated compressed gas cylinder, with $N_2H_5^+$. It is not clear whether this is due to their low reactivity or because they were lost on the surfaces of the cylinder or delivery lines, thus reducing the concentration reaching the reaction zone.

3.1.3. Other compounds or interferents

In the absence of a drift field, association product ions were observed for the reaction of $N_2H_5^+$ with methanol, ethanol, 3-hexenol, toluene, and acetic acid. However, a drift field of 20 $\mathrm{V\,cm^{-1}}$ was sufficient to inhibit the formation of these products. Surprisingly, 2-methyl-3-buten-2-ol reacted with $N_2H_5^+$ to form an ion with $m/z=101$, which is consistent with formation of a substituted hydrazine and elimination of water:



Scheme 4.

This was the only example of anything other than adduct formation with a non-carbonyl compound. No products were observed for the reaction of the reagent ion with heptane under any conditions. No interference was noted when air was introduced into the sample stream, i.e. no reactions occur with N_2, O_2, or CO_2. With water vapor in the sample stream, a small amount of the adduct, $N_2H_5^+ \cdot H_2O$, forms (<1% of the $N_2H_5^+$ signal).

3.2. Injured grass aldehyde emissions

When plant material is damaged, a series of C_6 alcohols, aldehydes, and esters are released [7,13,14].

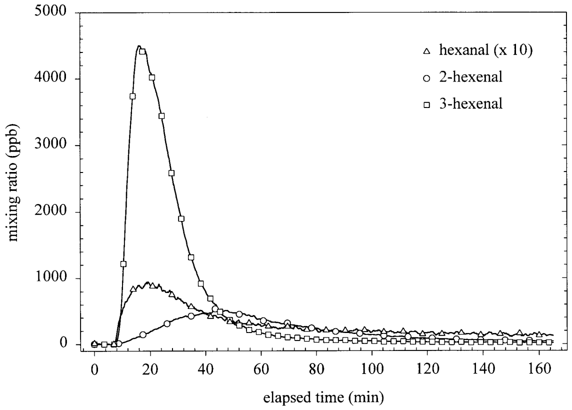


Fig. 2. Dynamic mixing ratio measurement of hexanal, 2-hexenal, and 3-hexenal emitted from frozen and thawed grass. Symbols (squares, circles, and triangles) on the plots have no significance and are used just to distinguish between the three C_6 aldehydes.

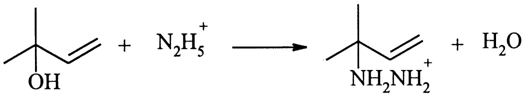
We focused on three of these compounds for quantification: hexanal, 2-hexenal, and 3-hexenal. Calibration bag samples provided us with the following ion signals (ion mass, ion chemical formula): hexanal (115, $C_6H_{12}N_2H_3^+$) 2.2 $\mathrm{hz\,ppb^{-1}}$; 2-hexenal (113, $C_6H_{10}N_2H_3^+$) 0.4 $\mathrm{hz\,ppb^{-1}}$, (131, $N_2H_5^+ \cdot C_6H_{10}O$) 1.9 $\mathrm{hz\,ppb^{-1}}$; 3-hexenal (113, $C_6H_{10}N_2H_3^+$) 1.6 $\mathrm{hz\,ppb^{-1}}$, (131, $N_2H_5^+ \cdot C_6H_{10}O$) 0.08 $\mathrm{hz\,ppb^{-1}}$, where the instrument sensitivity is given in units of ion counts per second (hz) per part per billion (ppb) of reagent gas. The distinctly different product distribution between 2- and 3-hexenal allowed us to selectively quantify these compounds using linear algebra. One minute averaging of baseline (high purity air) signal resulted in a background signal corresponding to a mixing ratio of ~0.5 ppb for each compound. With baseline noise of ~0.5 ppb (one standard deviation), the lower limit of detection was estimated to be about 1–2 ppb for each compound.

A time-series measurement of these three compounds from damaged grass is shown in Fig. 2. Each plot represents a 1 min running average of signals collected at ~10 s intervals. As the frozen grass warms, the first compounds to be detected are 3-hexenal and hexanal. These compounds appear in a burst whereas the emissions of 2-hexenal only slowly rise. As the grass sample becomes depleted in compounds, the emissions of all three compounds decrease. The time-integrated emissions over the experimental period were found to be: 4 $\mu g\ g^{-1}$ hexanal, 27 $\mu g\ g^{-1}$ 2-hexenal, 81 $\mu g\ g^{-1}$ 3-hexenal (normalized to the fresh grass sample mass).

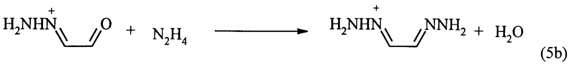
4. Discussion

This CIMS method is selective and resistant to interferences in air. Protonated hydrazine reacts selectively with carbonyl compounds (with the exception of 2-methyl-3-butene-2-ol) to form product ions that are distinctly identified with the analyte. Further studies are required to understand the product branching ratios of these reactions. For example, both 2 and 3-hexenal react to form protonated hydrazones and association products, but 3-hexenal forms far more of the protonated hydrazone. The close proximity of the double bond in 2-hexenal may inhibit the reaction to form the hydrazone.

There is evidence that the reaction to form the hydrazone involves neutral hydrazine [17]. We observed a double hydrazone product from the reaction of $N_2H_5^+$ glyoxal in the presence of neutral hydrazine. For this to occur, the initial protonated hydrazone [formed in Scheme 5 must have reacted with neutral hydrazine [in Scheme 6]



Scheme 5.



Scheme 6.

The solution phase chemistry of hydrazine with carbonyl compounds is initiated by donation of the free electron pair on nitrogen to the carbon atom of the carbonyl group, followed by migration of a proton from the nitrogen to the carbonyl oxygen [20]. Subsequently, the OH group is protonated from solution and splits off as water. The reaction is completed when the last proton on the reacting nitrogen is released into solution, and a double bond forms between the nitrogen and the carbon. Thus, the overall solution reaction is acid catalyzed. In our gas phase system, it may be sterically or geometrically difficult for the protonated hydrazine to both attach to the carbon and protonate the oxygen. Instead, it is likely that $N_2H_5^+$ shares a proton with oxygen first, and a neutral hydrazine attacks the carbon. To understand this phenomenon, we are actively pursuing studies to determine the mechanism of hydrazone formation in the gas phase [17].

It is intriguing that a reaction takes place between 2-methyl-3-butene-2-ol (MBO, an important emission product from plants [21]) and protonated hydrazine. The alcohol (OH) group is attached to a tertiary carbon, perhaps making the alcohol more reactive. This is because the tertiary carbon makes a very stable carbocation. The product of this reaction has the same mass to charge ratio as the protonated hydrazone of pentanal. Thus, it may be difficult to distinguish these two compounds.

The association products of organic compounds and $N_2H_5^+$ are somewhat fragile in the presence of the drift field. We observed that higher intensity electric fields (>20 V cm^{-1}) dissociate association products for all compounds, including carbonyls. However, the protonated hydrazones appear to be quite stable. This finding suggests a method for identifying a variety of noncarbonyl compounds as well as distinguishing isomers of carbonyl compounds in a single instrument. In a strong field (>35 V cm^{-1}), only the protonated hydrazones are detected. As the field strength is reduced, association products will persist and are detected. By comparing the branching ratios of the pure compounds at these field strengths to those detected in the sample stream, a precise identification of the analytes may be obtained.

Qualitatively, the products observed in the grass wounding experiment are consistent with the results from proton transfer experiments (see Fig. 2 of Fall et al. [13]). In these experiments, 3-hexenal was identified as the major initial aldehyde emitted, with 2-hexenal rising more slowly later. This behavior is consistent with mechanisms outlined for the peroxidation of linolenic acid present in plant material (see Fig. 1 of Fall et al. [13]). Linolenic acid peroxidation first forms 3-hexenal, which is then isomerized to 2-hexenal. Hexanal is the product of the peroxidation of linoleic acid. Both 3-hexenal and hexanal are formed by the same peroxidation process (but starting with different fatty acids). Thus the dynamic emission rates should follow a similar curve in time. Indeed, the shape of the time series plot of the chamber concentration of hexanal is similar to that of 3-hexenal.

The relative mass emission rates of hexanal, 2-hexenal and 3-hexenal were 4:24:72 (summing to 100), respectively. These relative emission rates compare favorably to those calculated from measurements of headspace samples of freshly harvested fescue [22] (3:34:63) and measurements of headspace samples of perennial rye grass [23] (7:34:58).

The efficacy of this method for quantitative analysis of wide variety of air samples is still to be confirmed. We are presently investigating the physical chemistry of the reaction of $N_2H_5^+$ with carbonyl and other compounds in a SIFT-CIMS reactor [17]. This course of study should provide both kinetic and mechanistic information that we can use to improve the sensitivity and selectivity of the reaction. For example, by measuring the binding strength of a noncarbonyl compound clustered with the hydrazinium ion, we will be able to determine the strength of a drift field necessary to reduce these cluster ions below detectable levels. The product branching ratio (protonated hydrazone versus adduct) has been shown to be useful in identifying isomers. We hope to uncover the mechanism that results in these branching ratios. Also, evidence of the reaction of MBO with $N_2H_5^+$ to eliminate water suggests that there may be other, non-carbonyl, species that react similarly. Although the reaction mechanism may be more complex than that of other analytical CIMS techniques (e.g. proton transfer, charge transfer) the general specificity for carbonyl compounds in a single system makes it a valuable addition to the CIMS toolkit.

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